

3 V and 4 V lithium manganese oxide cathodes for rechargeable lithium batteries

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Abstract

Two lithium manganese oxide materials based on the spinel structure have been synthesised by a new solution method which has the advantage that it can be carried out in air unlike previous sol-gel methods. One material is suitable as a 3 V and the other as a 4 V cathode in rechargeable lithium cells. In the case of the 3 V material the addition of a small amount of carbon to the solution during preparation yields a material with a significantly enhanced cycling performance. Cycling at discharge and charge current densities of 1 and 0.5 mA cm⁻², respectively (corresponding to a discharge rate of C/2) and between 3.7 and 2.0 V yields a capacity of 90 mAh g⁻¹ after 300 cycles for the material prepared using carbon. This represents an enhancement of the discharge capacity by 50% on the 300th cycle when compared with the same material without carbon. Cathodes fabricated from the 4 V material have been cycled at discharge and charging current densities of 1 and 0.5 mA cm⁻², respectively (corresponding to a discharge rate of C/2) between limits of 4.4 and 3.3 V. The specific discharge capacity obtained initially is 110 mAh g⁻¹ decreasing to 85 mAh g⁻¹ at 300 cycles.

Keywords: Rechargeable lithium batteries; Cathode; Lithium; Manganese oxide

1. Introduction

The spectacular developments which have taken place in the area of microelectronics over the past twenty years have led to massive improvements in the performance of electronic devices per unit weight and volume of the device; the same has not been true in the field of batteries. Improvements in microelectronics have led to a very significant reduction in the size and weight of many portable consumer electronic products such as mobile telephones, laptop computers and camcorders to the point where the battery now represents a major factor limiting further product development in these multi-million dollar industries. In a different field, antipollution legislation is forcing the pace of electric vehicle development which is in turn critically dependent on advances in battery technology. Rechargeable lithium batteries represent the best technology for future portable electronic products and electric vehicles since they possess the highest volumetric and gravimetric energy density of any rechargeable battery system leading to a substantial reduction in the size and weight of power sources as well as an increase in the energy stored.

Rechargeable lithium batteries are now a commercial reality with the launch of the Sony cell [1]. This system consists of a carbon anode, LiCoO₂-based cathode and a liquid electrolyte. The substitution of carbon for lithium as the anode demands the use of cathodes with potentials of about 4 V versus Li⁺/Li to offset the otherwise lower cell potential. It is to be hoped that this cell, which offers a leap forward in battery performance, is just the beginning of the long-awaited revolution in advanced batteries. Currently, systems based on metallic lithium as well as carbon anodes are being explored. As a consequence, there is considerable interest worldwide in developing both 3 V and 4 V cathodes. The candidate cathode materials are based mainly on cobalt, nickel, vanadium or manganese oxides. The manganese oxides offer very considerable advantages compared with oxides containing the other three elements in that manganese is substantially cheaper and less toxic, both aspects are crucial to a consumer product for the 21st century. It is widely acknowledged that lithium manganese oxides represent attractive materials from which to fabricate cathodes for rechargeable lithium batteries [2]. Several lithium manganese oxide materials have been investigated as possible cathodes for such batteries including Li₂Mn₄O₉, Li₄Mn₅O₁₂, CDMO (which is composed of γ/β -MnO₂ and lithiated

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spinel) and lithium-ion exchanged MnOOH [2–5]. The first to be discovered was LiMn_2O_4 into which up to one lithium per formula unit can be reversibly inserted at an open-circuit potential of 3 V versus Li^+/Li [6,7]. Most of the lithium can also be reversibly removed from LiMn_2O_4 and this process is associated with an open-circuit potential of 4 V versus Li^+/Li [8]. The original LiMn_2O_4 material was prepared by high temperature solid-state reaction and although possessing a satisfactory theoretical specific capacity and open-circuit voltage, the practical capacity declined markedly on cycling. Lower temperature routes, often involving sol-gel methods were developed in an effort to improve cycling performance [9–12]. The challenge in cathode development for rechargeable lithium batteries, whether based on metallic lithium or carbon anodes, is to produce a lithium manganese oxide material which can be cycled many times, to deep discharge, with excellent capacity retention and at relatively high current densities. This challenge exists for both liquid and solid polymer electrolytes. Many of the most promising polymer electrolytes currently being developed contain a high proportion of low molecular weight solvents, e.g. propylene carbonate (PC) and ethylene carbonate (EC), as such they bear some similarity to liquid electrolytes. It is therefore important to first demonstrate cathode performance in the liquid systems which form an important component of polymer electrolytes, before considering the polymer electrolytes themselves. Differences between cathode performance in liquid and plasticised polymer electrolytes should then be mainly confined to factors arising from the host polymer or additives contained therein. The important role of the interface between polymer electrolytes and intercalation cathodes on the performance of polymer electrolyte batteries has been highlighted by one of the authors previously [13–15]. In this paper we report the synthesis, by a new solution route, of two lithium manganese oxide materials based on the spinel LiMn_2O_4 , one suitable for use as a 3 V and the other as a 4 V cathode [16,17]. Results are presented of cycling experiments on composite cathodes which indicate the promising performance of these materials.

2. Synthesis and characterisation of active materials

2.1. 3 V material

$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99+%) was added to a solution of Li_2CO_3 (BDH, 99.5%) in distilled water. Sufficient manganese(II) acetate was used to yield a 2:1 mole ratio of manganese to lithium. A small amount of carbon was introduced into the mixture which was then subjected to vigorous stirring. A precipitate formed, the remaining water being removed first by rotary

evaporation at 85 °C followed by heating at 200 °C for 4 days. There are two main advantages of this synthesis. First, the use of such a low temperature makes this route particularly attractive for low-cost large-scale manufacture of the materials. Second, our synthetic procedure can be carried out in air unlike some sol-gel methods which are based on LiOH instead of Li_2CO_3 and thus require inert atmospheres [10].

In order to study the influence of carbon on the properties of the electrodes some materials were prepared exactly as described above but without the addition of carbon during the synthesis. The resulting powders were analysed by X-ray diffraction using a Philips diffractometer operating with $\text{Cu K}\alpha$ radiation. The powder patterns for materials with and without carbon are very similar, Fig. 1(a) and (b). Both exhibit broad peaks which are indicative of a small particle size. The patterns are consistent with a spinel structure and there is no evidence of any additional peaks in the X-ray patterns arising from other phases. The oxidation states of the lithium manganese oxide spinels were determined by a sequence of redox titrations involving the $\text{MnO}_4^-/\text{Mn}^{2+}$, $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples and following the procedure described by Vetter and Jaeger [18]. This process yielded a composition $\text{LiMn}_2\text{O}_{4.1}$ for both materials, this is indicative of a defect spinel with

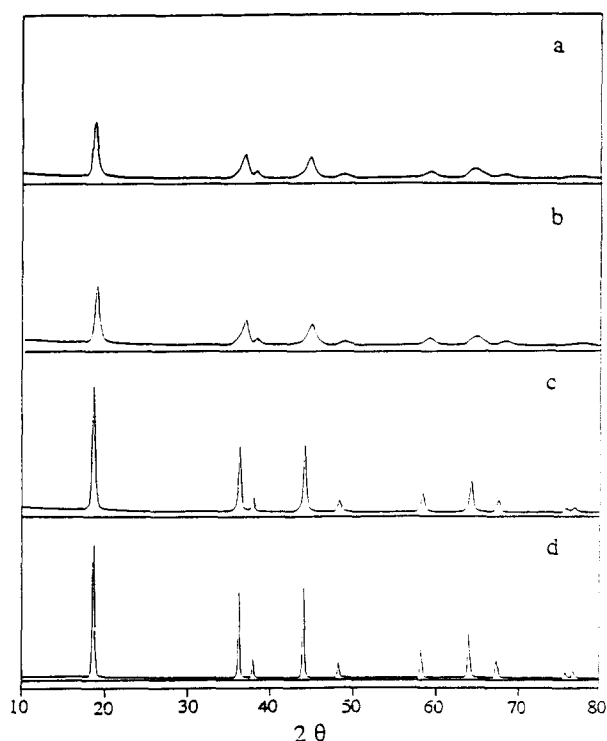


Fig. 1. Powder X-ray diffraction patterns for lithium manganese oxide spinels; (a) $\text{LiMn}_2\text{O}_{4.1}$ synthesised from solution then fired at 200 °C; (b) $\text{LiMn}_2\text{O}_{4.1}$ synthesised from solution with carbon then fired at 200 °C; (c) LiMn_2O_4 synthesised from solution then fired at 600 °C, and (d) synthesised by solid-state reaction between Li_2CO_3 and Mn_2O_3 at 850 °C.

a higher average oxidation state than the stoichiometric LiMn_2O_4 prepared at high temperatures.

2.2. 4 V material

A similar solution-based synthetic procedure was adopted for the preparation of the high voltage material, the main difference being the use of a higher firing temperature. X-ray diffraction confirmed the spinel-like nature of the 4 V compound, Fig. 1. The peak widths lie between those of the low-temperature 3 V material and LiMn_2O_4 prepared by conventional high temperature solid-state reaction at 850 °C, Fig. 1(d), this is indicative of a particle size which is intermediate between these two extremes. Oxidation state analysis of the 4 V material revealed a composition very close to that of the stoichiometric spinel LiMn_2O_4 .

3. Cell assembly and testing

Composite cathodes were fabricated in a similar manner for both 3 V and 4 V materials by dry mixing the appropriate lithium manganese oxide, carbon black and polytetrafluoroethylene (PTFE) in the weight ratio 80:13:7. The mixtures were pressed on to aluminium and stainless-steel grids in the case of the 3 V and 4 V materials respectively, typically with a loading of 17 mg cm^{-2} , and the entire assembly was then dried under a vacuum at 80 °C for 12 h. Three-electrode cells were constructed from the composite cathodes, lithium metal reference and counter electrodes. For the 3 V cathode the electrolyte consisted of a 1 M solution of LiAsF_6 (LITHCO) dissolved in PC (Aldrich 99+ %). The salt was used as received but the PC was rigorously purified using a Fischer HMS 500 C distillation apparatus with 90 theoretical plates. In the case of the 4 V cathode a 1 M solution of LiClO_4 in our rigorously purified PC was employed, the salt was dried under vacuum at 150 °C overnight before dissolution in the solvent. In both cases, the electrolyte was soaked into Whatman GF/F filter pads which acted as separators between the electrodes. All manipulations of air-sensitive materials as well as the cell assembly were carried out in a MBraun argon-filled glove box from which H_2O and O_2 are continuously removed.

By introducing a third (reference) electrode into the cell, cycling of the composite cathode could be carried out in isolation, i.e., without influence from the lithium metal anode [19]. Cycling studies were carried out using a Sycopel Scientific Multistat under the control of an IBM PC. All measurements were carried out at 25 °C.

4. Results and discussion

4.1. 3 V cathode

Cycling of the composite cathodes was carried out galvanostatically between 3.7 and 2.0 V with respect to the lithium metal reference, and at discharge and charge currents of 1 and 0.5 mA cm^{-2} , respectively, the discharge rate was $C/2$. The specific discharge capacities for each cycle are presented in Fig. 2, these are based on the weights of lithium manganese oxide in the composite cathodes. In the case of the lithium manganese oxide prepared with carbon (less than 1 wt.%), the initial capacity is in excess of 140 mAh g^{-1} compared with a theoretical capacity for $\text{LiMn}_2\text{O}_{4.1}$ of 176 mAh g^{-1} and rises slightly within the first few cycles subsequently falling to 125 mAh g^{-1} at 100 cycles, 100 mAh g^{-1} at 200 cycles, and 90 mAh g^{-1} at 300 cycles.

Although the initial cycling behaviour for the material prepared without carbon is very similar to that with carbon, the capacity fade is significantly greater in the absence of carbon. The material prepared with carbon possesses a capacity some 30 mAh g^{-1} greater than the material without carbon at 300 cycles. This corresponds to an enhancement of 50% indicating the very significant improvement in cycling performance which can be obtained if less than 1% of carbon is added to the solution during synthesis of the lithium manganese oxide spinel. One possible origin of the enhanced cycling behaviour is better electronic conductivity of the new material due to incorporation of carbon during the synthesis. To test this, pellets of each material were prepared and their conductivities measured by a.c. impedance methods. Both materials yield almost identical conductivities of $10^{-6} \text{ S cm}^{-1}$ at 30 °C indicating that the origin of the improved performance does not arise from better conductivity. The compositions and X-ray diffraction patterns of the two

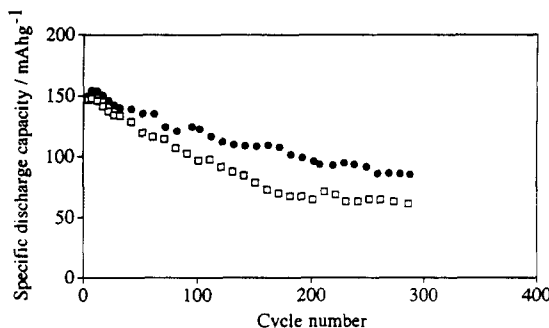


Fig. 2. Variation of specific discharge capacity with the number of cycles for the 3 V composite cathodes containing, $\text{LiMn}_2\text{O}_{4.1}$ synthesised from solution at 200 °C with (●) carbon and (□) without carbon. Cycling was carried out galvanostatically at discharge and charge current densities of 1 and 0.5 mA cm^{-2} , respectively, and between 3.7 and 2.0 V. The discharge rate was $C/2$.

materials do not offer an answer to the difference in cycling performance; further investigations are continuing in order to better understand the role of carbon. Fig. 3 indicates the influence of varying the amount of carbon added during the synthesis on the cycling performance. These results refer to 3 V material prepared by the sol-gel route [10] however as is the case for our solution synthesis, enhanced cycling is obtained when carbon is added during the sol-gel synthesis. The construction of the composite cathodes and the cycling experiments were carried out as described above. It is evident that the optimum amount of carbon is approximately between 1 and 3 wt.% of the active material and that the broad maximum moves from 1 to 3% with increasing cycle number.

The effect of varying the charge/discharge current on the specific capacity is shown in Fig. 4. The cell and the cutoff potentials were identical to those used to collect the data for Fig. 2. In the case of the discharges carried out at 0.25 and 0.5 mA cm⁻² equal charge and discharge currents were employed, however when the cell was discharged at 1 mA cm⁻², a charging current of 0.5 mA cm⁻² was imposed. The specific discharge capacities presented in Fig. 4 are an average of the first four cycles in each case. Under this charge and

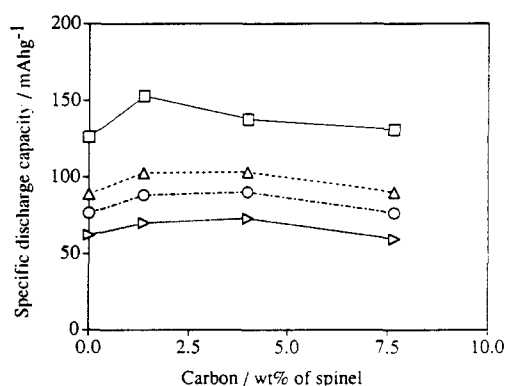


Fig. 3. Influence of the quantity of carbon added during the sol-gel preparation of 3 V lithium manganese oxide on the specific capacity: (□) 1st cycle; (△) 32nd cycle; (○) 52nd cycle, and (◇) 104th cycle.

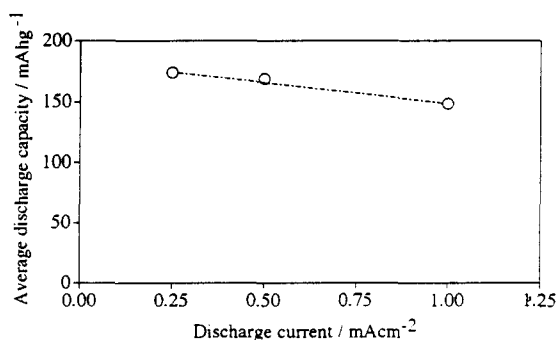


Fig. 4. Influence of current density on the specific capacity of the 3 V composite cathode containing LiMn₂O_{4.1} synthesised from solution at 200 °C with carbon. The capacities are averages taken over the first four cycles in each case.

discharge regime the average capacity declined linearly with increasing discharge current. It is interesting to review the progress that has been made in improving the cycling performance of lithium manganese oxide spinels over recent years. This is summarised in the histogram plot, Fig. 5. We do not claim that this Figure includes the results of all the materials which have been prepared by different groups but it does give an impression of the improvements which have accrued in moving from high-temperature solid-state synthesis to a sol-gel method with and without carbon (sol-gel + C and sol-gel, respectively, in Fig. 5) and then to a solution-based preparation with and without carbon at 300 and 200 °C. The specific discharge capacities presented in this Figure are again averaged over the first four cycles although they also reflect the trends at higher cycle number. It is evident from the Figure that very substantial improvements in cycling performance have been achieved. At the higher discharge rate of C/2 the capacity has been doubled in changing from the high-temperature solid-state synthesis to the solution method at 200 °C with carbon. Increasing the discharge rate from C/4 to C/2 severely diminishes the capacity of the solid-state material whereas the material prepared from solution with carbon at 200 °C possesses a capacity which is much less sensitive to discharge rate. The improvement in performance obtained by reducing the firing temperature from 300 to 200 °C for the material prepared by the solution route is evident. This is due mainly to the reduction in particle size and hence increase in surface area upon firing at a lower temperature, which is apparent in the broader peaks observed in X-ray diffraction patterns of the 200 °C material.

4.2. 4 V cathode

Before embarking on cycling tests in the 4 V region it is important to establish that the electrolyte is suf-

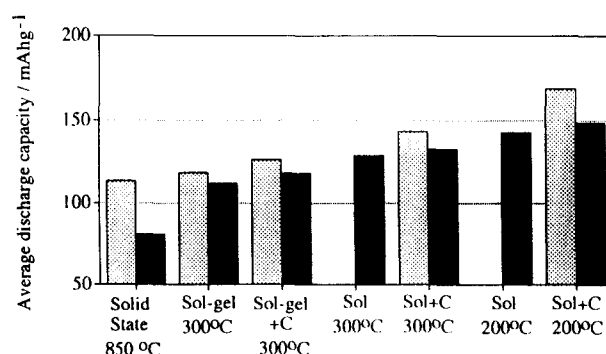


Fig. 5. Histogram plot comparing the cycling performance of several 3 V composite cathodes containing lithium manganese oxide spinels prepared under different conditions. The composite cathodes and cycling conditions were identical in all cases, the only difference being the active material. The specific capacities are an average taken over the first four cycles. The charging rate is C/4 and the discharge rates are (▨) C/4 and (■) C/2.

ficiently stable at the highly oxidising potentials required for charging the composite 4 V cathode. The variation of current with potential obtained from a linear voltammetric measurement, in which the potential is swept at a rate of $10 \mu\text{V s}^{-1}$ for a three-electrode cell in which the working electrode is the composite 4 V cathode described above (with an area of 0.9 cm^2), is shown in Fig. 6. The results were obtained using a Biologic Macpile. The current remains modest on a fully charged electrode up to 4.4–4.5 V versus Li^+/Li . The cycling performance of composite cathodes fabricated from our 4 V LiMn_2O_4 material, with and without the addition of carbon during the synthesis, is presented in Fig. 7. In both cases cycling was carried out galvanostatically between 4.4 and 3.3 versus Li^+/Li and at discharge and charging current densities of 1 and 0.5 mA cm^{-2} , respectively, the discharge rate was again $C/2$. Capacities are quoted per gram of the active material. It is evident that the use of carbon in the synthesis has no effect on the cycling performance of the 4 V material in complete contrast to the 3 V cycling described in the previous section. The initial discharge capacity is 110 mAh g^{-1} , rising very slightly on the second cycle, then declining by only 10 mAh g^{-1} to 100 mAh g^{-1} at 100 cycles, 90 mAh g^{-1} at 200 cycles and 85 mAh g^{-1} at 300 cycles. This represents very good capacity retention particularly in view of the

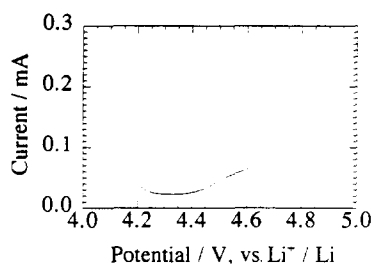


Fig. 6. Electrochemical stability of a 1 M solution of LiClO_4 in rigorously purified propylene carbonate when in contact with a charged 4 V composite cathode based on LiMn_2O_4 .

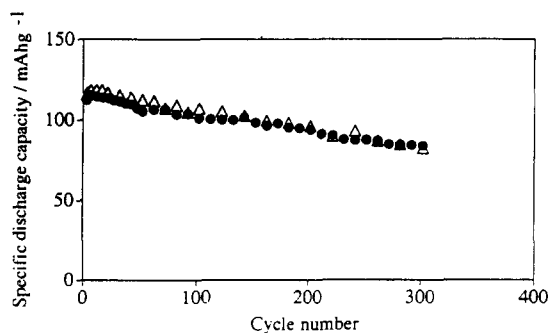


Fig. 7. Variation of specific discharge capacity with the number of cycles for 4 V composite cathodes containing, LiMn_2O_4 synthesised from solution at $600 \text{ }^\circ\text{C}$ with (●) carbon and (Δ) without carbon. Cycling was carried out galvanostatically at discharge and charge current densities of 1 and 0.5 mA cm^{-2} , respectively, and between 4.4 and 3.3 V. The discharge rate was $C/2$.

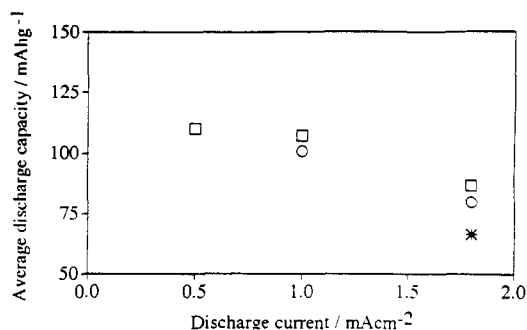


Fig. 8. Influence of the current density on the specific capacity of the 4 V composite cathode. Cutoff potentials are those used in Fig. 7 and the capacity is averaged over the first four cycles. Charging currents: (□) 0.5 mA cm^{-2} ; (○) 1 mA cm^{-2} , and (*) 1.8 mA cm^{-2} .

relatively high current densities and depth-of-discharge. The effect of varying the discharge and charging currents on the specific discharge capacity is presented in Fig. 8. Three different discharge and charging currents 0.5 , 1 and 1.8 mA cm^{-2} were considered. The specific discharge capacities again represent the average obtained from the first four cycles. The overall trend is towards a lower discharge capacity at high charge or discharge currents although, when cycling at lower current densities, the influence of varying the magnitude of the current density on the discharge capacity is less than at high current densities. Attempts to cycle the 4 V LiMn_2O_4 cathode in the 3 V region yielded inferior results to the $\text{LiMn}_2\text{O}_{4.1}$ cathode prepared at $200 \text{ }^\circ\text{C}$ with carbon, corresponding attempts to cycle the $\text{LiMn}_2\text{O}_{4.1}$ cathode at 4 V proved equally unsatisfactory. Therefore, despite the fact that both the 3 V and 4 V materials have similar spinel structures, their performance as cathodes for rechargeable lithium batteries is markedly different.

It is interesting to compare the cycling performance of the 3 V and 4 V materials when cycled within their own voltage regimes, Figs. 2 and 7. The capacity retention of the 4 V material is significantly superior to that of the 3 V; this may be attributed to the cubic to tetragonal phase change which occurs in the latter case. X-ray data confirm that upon cycling the 3 V material the amount or residual cubic phase present at the end of each discharge increases on cycling whereas the 4 V material remains cubic throughout.

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