

Lithium metal rechargeable cells using Li_2MnO_3 as the positive electrode

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Abstract

Rechargeable lithium cells have been fabricated using Li_2MnO_3 as the positive electrode, lithium metal as the negative electrode and 1 M LiAsF_6 in DMC/EC (1:1 v/v) as the electrolyte. Charge/discharge behaviour was evaluated and the cells showed improved performance after the first five cycles. The cells could be cycled at least 15 times without loss in capacity. Similar electrochemical trends were observed with LiPF_6 in a EC/DEC mixture. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In recent years, intensive attention has been focused on to the development of positive electrode materials for use in lithium batteries based on lithiated manganese oxides because of their low cost and environmental benignity [1]. LiMn_2O_4 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$ [2] and the layered LiMnO_2 [3] are some of the compounds to mention.

However, to our knowledge, no electrochemical study has so far been reported to demonstrate the usefulness of the Li_2MnO_3 as a positive electrode material in rechargeable lithium batteries. It is rather interesting to note that some of its derivatives which are obtained after acid leaching (e.g., $\text{Li}_2\text{Mn}_4\text{O}_9$ and the layered MnO_2) [4] have been examined for their activity as potential cathodes in rechargeable lithium cells. Hence, we decided to carry out a systematic investigation of the synthesis as well as electrochemical behaviour of Li_2MnO_3 . We report in this paper a new and simple route for preparing Li_2MnO_3 and its utility as a positive electrode in rechargeable lithium batteries.

2. Experimental

Manganese acetate (E. Merck, 99.9% India) and lithium acetate (AR, SRL, India), LiAsF_6 and LiPF_6 , (Aldrich,

99%) were used as received. Dimethyl carbonate [DMC] (Spectrochem, India), diethyl carbonate [DEC] (E. Merck, Germany) were distilled over P_4O_{10} in a dry nitrogen atmosphere before use. Ethylene carbonate [EC] (E. Merck, Germany) was stored over molecular sieves (4 Å, which had been dried at 200°C) under a reduced pressure of 0.1 mm Hg for 5 h.

2.1. Preparation of Li_2MnO_3

Manganese acetate was heated with 2 molar equivalents of lithium acetate at 800°C for 3 h and annealed at room temperature. The resulted red solid was confirmed as Li_2MnO_3 from its X-ray powder pattern [4,5].

2.2. Instrumentation

X-ray measurements were carried out using JEOL JDX 8030 equipment with Cu-K α radiation ($\lambda = 1.5406$ Å). TGA was performed with a STA 1500 PL from Thermal Sciences.

2.3. Fabrication of the cell

The lithium manganate powder prepared as described in Section 2.1, was mixed with 2% PVDF and 10% graphite and coated over aluminium foil which was used as a cathode. Coin-type (2016 size) cells were assembled using lithium metal as the anode and 1 M LiAsF_6 in an EC/DMC

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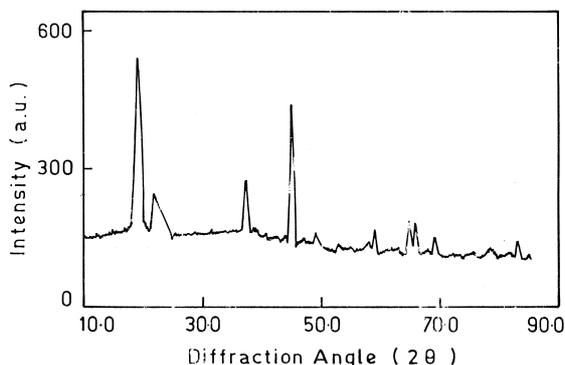


Fig. 1. X-ray diffraction pattern for Li_2MnO_3 synthesized at 800°C .

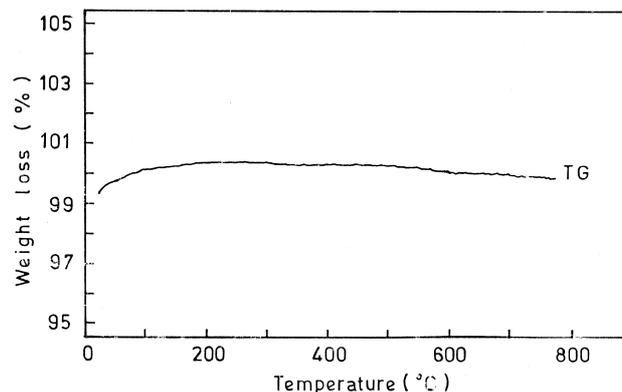


Fig. 2. Thermogravimetric curve of Li_2MnO_3 . Rate of temperature rise: 5°C per minute, in air.

(1:1 v/v) mixture as the electrolyte, soaked in a polypropylene separator. The cells were assembled in an argon-filled M Braun dry box. Charging and discharging of the cells were carried out galvanostatically at 0.1 mA.

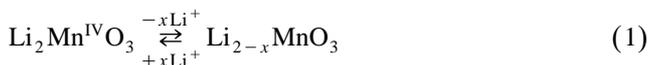
3. Results and discussion

The X-ray powder pattern (Fig. 1) of Li_2MnO_3 prepared as in Section 2.1 showed sharp peaks revealing its high crystallinity. That there were no peaks due to inorganic metal oxides was indicative of its pure phase. The unit cell parameter calculated from the XRD data, assuming cubic settings agreed well ($a = 8.12 \text{ \AA}$) with that reported in the literature [6].

The TGA curve is shown in Fig. 2. That there was no appreciable weight loss in the TGA up to 800°C further confirmed its purity. This compound can also be prepared from the respective nitrates [7] and [8]. However the material obtained from the acetate route was used in this study for determining its battery activity. It is to be

emphasized that previously reported methods of preparation employed higher temperatures and longer hours of heating [4,6].

Coin type cells were assembled with Li_2MnO_3 as the cathode and Li metal as the anode as mentioned above. The open circuit voltage immediately after assembling was found to be 2.8 V which did not show any variation on standing, even after 2 days. This indicated the stability of the cathode material and that there is no self-discharge. On charging at a constant current of 0.1 mA, the cell voltage increased rapidly to 4.5 V in ca. 5 min. The same trend was observed during discharge, where a voltage of 2.5 was reached in ca. 5 min. This probably is due to the slow equilibrium reaction of charge/discharge (Eq. (1)) under a heavy current.



However, it was noticed that the rate of charge/discharge gradually decreased with the increase in the number

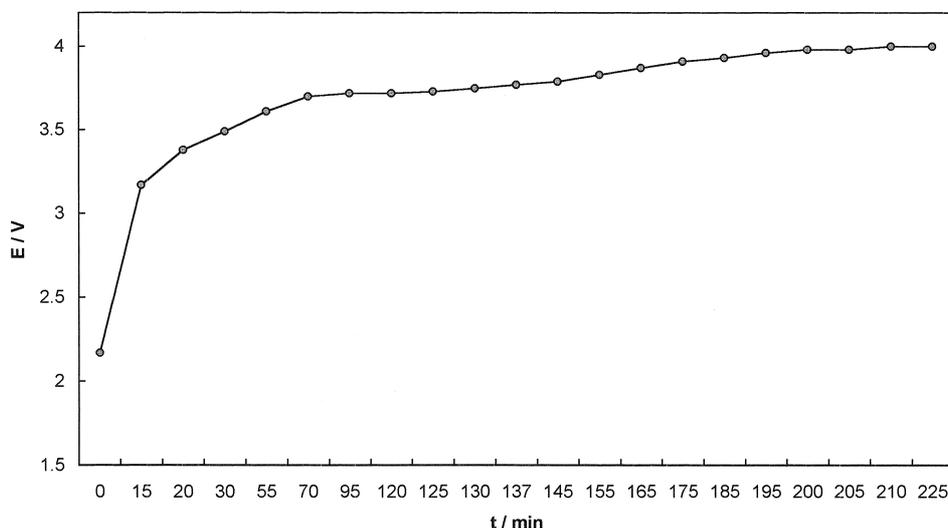


Fig. 3. Galvanostatic charging curve of the $\text{Li}/\text{Li}_2\text{MnO}_3$ cell (2013 size) at 0.1 mA.

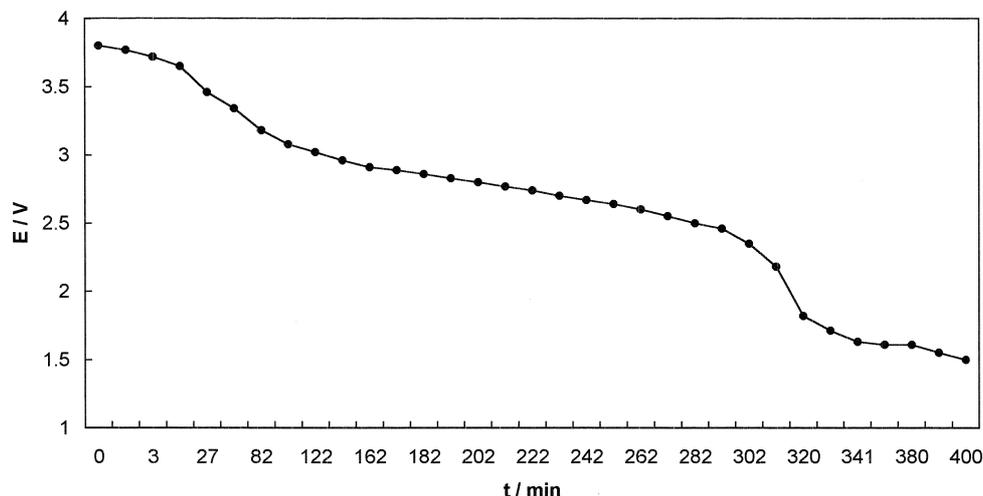


Fig. 4. Galvanostatic discharge curve of the Li/Li₂MnO₃ cell (2013 size) at 0.1 mA.

of cycles repeated as above which stabilized after five cycles. Typical charge/discharge curves, obtained at the 13th cycle, are shown in Figs. 3 and 4, respectively. The Li/Li₂MnO₃ cell was charged at a current of 0.1 mA (Fig. 3) and discharged at the same rate (Fig. 4). The discharge curve showed a plateau in the region 3 to 2.5 V. The capacity in this region was calculated to be 10.6 mA h g⁻¹. Similar behaviour was observed in the case of LiPF₆ as well as in EC/DEC mixture. It is to be mentioned here that Li₂MnO₃ was reported to be electrochemically inactive for lithium ion insertion/deinsertion [6].

From the nature of the charge/discharge curves it is evident that Li₂MnO₃ can be used as a 3 V reversible positive electrode. This is conceivable as the manganese is in the higher IV oxidation state, a fact which is supported by earlier reports that even a slight increase in the average oxidation state of manganese in Li₂MnO₄ (from 3.5) resulted only in a 3 V reversible cathode [9].

Attempts to discharge the cell below 2.5 V (where a steep fall in the potential was observed) were successful, as indicated by the second plateau region in Fig. 4, but the cell could not thereafter be recharged. This may be due to the reduction of the Mn^{IV} in Li₂MnO₃ to Mn^{III}, forming a compound Li_{2+x}MnO₃ (Eq. (2)):



Due to the Jahn–Teller effect distorting the symmetry from cubic to tetragonal phase, this results in the failure of the reversibility of the electrode and hence the cell [9]. This hypothesis needs to be proved by XRD, XPS and other measurements.

The discharge/charge coulombic efficiency was found to be fairly good, ca. 80%, but the capacity of the electrode was found to be low. This perhaps is due to the instability of the Mn^V formed out of the charging reaction which

prevents further de-intercalation of lithium. However, stable Mn^V complexes have been reported with bulky ligands [10]. Addition of complexing agents like acetyl acetone, triethanolamine, etc. to the electrolyte are expected to stabilize the Mn^V, which could cause more lithium ion to get de-intercalated from Li₂MnO₃ during charging thereby increasing the capacity of the electrode. Further investigations on this cathode material in this direction are in progress.

4. Conclusion

Li₂MnO₃ has been prepared by a simple route in a short duration of time. The resulting compound is purely crystalline with a smaller particle size. For the first time, this material has been shown to be useful as a 3 V, positive, electrode. Its discharge/charge coulombic efficiency is good at the fairly high current of current density of 0.05 mA cm⁻² when tested in 2016 sized cells. A plateau region is observed in the discharge curve for a sufficiently long time both in the case of LiAsF₆ and LiPF₆ as electrolytes. Experiments to increase its capacity are in progress.

Acknowledgements

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