

Li_{0.3}MnO₂—cathode material for secondary lithium batteries

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Abstract

Li_{0.3}MnO₂ synthesized by solid state reaction of CMD Faradizer M and LiOH or LiNO₃ as lithiating agents, in atmosphere or with the addition of oxygen and in the temperature range 375–450°C, has been investigated. Optimizing the synthesis route, a product with more than 30 m²/g specific surface area (SSA) was successfully synthesized and evaluated as positive electrode material in lithium cells. High charge–discharge rates up to C/2 have been applied to carry out the electrochemical performances in laboratory test cells with Li reference electrode. Real coin cells CR2032 have been assembled and tested and demonstrated an energy density of about 400 mWh/g. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Li_{0.3}MnO₂; Cathode; Lithium battery

1. Introduction

Since the beginning of the 1990s, manganese dioxide became the most investigated material for lithium secondary cells. Many attempts have been made to elucidate the factors influencing the rechargeability and the cyclability of MnO₂ and to improve its electrochemical characteristics. The appearance of cathode materials with high energy density based on lithiated transition metal oxides such as Co, Ni or Mn and high discharge voltage of 4 V, shifted the main interest to them. But the problems arose faster: oxidation of the electrolyte due to the high operation potential dissolution of some active cathode materials, fast self discharge, etc.

The aim of the present work is to demonstrate the energy characteristics and the advantages of Li_{0.3}MnO₂ synthesized under optimum conditions.

2. Experimental

In a series of papers [1–5] the investigation of different standard IBA samples as composite cathode materials in

primary Li/MnO₂ cells was described. We found some interesting correlations between physicochemical characteristics and electrochemical behavior of the tested manganese dioxides. The specific surface area (SSA) plays the most important role in the electrochemical behavior of the cathode materials—the higher the SSA the larger the discharge capacity at high current drains and low temperature [2]. Ilchev et al. [1] have shown that the optimum temperatures of pretreatment of various manganese dioxides differ and is related to their nature, CMD or EMD. In Refs. [2–4] for the first time we have demonstrated that the thermal pretreatment of manganese dioxide used in lithium cells must be taken also into account. Yoshio et al. [8] have shown the optimum conditions of synthesis of lithiated manganese dioxides synthesized from EMD precursor. In Refs. [4,5] we have shown on the basis of electrochemically lithiated nonstandard manganese dioxide CMD samples, (kindly supplied by SEDEMA) that the reversibility of secondary manganese dioxides also depends on the SSA of the samples and on the content of foreign ions [3].

The lithiated MnO₂ samples were prepared by the classical solid-state reaction according to the method and optimized conditions of synthesis described in Refs. [6–8]. A final temperature of pretreatment in the range of 375–450°C was chosen. The synthesized product (later named as sample A) has the chemical formula Li_{0.3}MnO₂ and SSA, measured by nitrogen absorption method BET, in the range of 10–12 m²/g. It is necessary to mention that the

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starting manganese dioxide precursor, CMD Faradizer M has SSA of $105 \text{ m}^2/\text{g}$. Applying a new multistep technique, we succeeded in synthesizing the same product $\text{Li}_{0.3}\text{MnO}_2$ but with SSA larger than $30 \text{ m}^2/\text{g}$ (later named as sample B). The process consists of mixing and reacting well-dried products. First, the starting precursor (CMD Faradizer M) is thermally pretreated at 350°C for 12 h without lithiating agent to remove the adsorbed and chemically bonded water. The used lithiating agent LiOH or LiNO_3 must also be well dehydrated, with moisture less than 500 ppm. The intimate mixture of the precursor and lithium salt is prepared in a dry glove box under argon atmosphere with moisture content less than 25 ppm in a ball mill. Thus, the prepared mixture is reacted in a Pt crucible at 250°C for 24 h, at 350°C for 24 h, and finally fired at 450°C for 8 h. The synthesized product is with chemical formula $\text{Li}_{0.3}\text{MnO}_2$ and SSA in the range of $28\text{--}32 \text{ m}^2/\text{g}$. The test electrodes were prepared as previously described in Refs. [3–5] and subjected to different current drains. A three-electrode test cell with lithium reference electrode and limited electrolyte volume was used. The electrolyte in use was 1 M LiClO_4 in PC:DMC, 1:1 by volume.

3. Results and discussion

Fig. 1 represents the XRD data of the starting precursor CMD manganese dioxide FARADIZER M and the lithiated product obtained from it. The final product has an SSA of $10 \text{ m}^2/\text{g}$ for sample A and $30 \text{ m}^2/\text{g}$ for sample B,

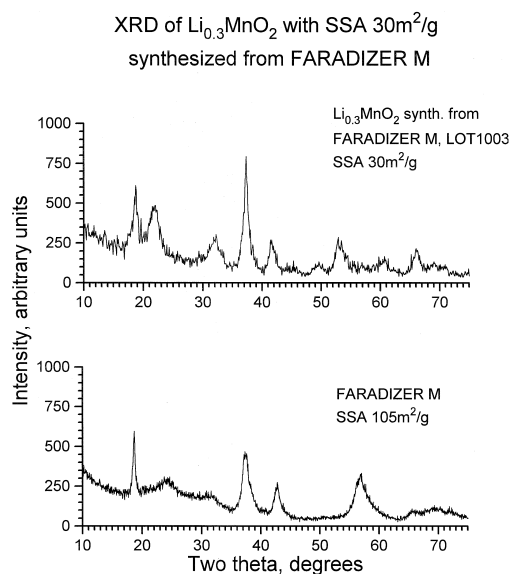


Fig. 1. XRD patterns of starting precursor CMD Faradizer M with SSA $105 \text{ m}^2/\text{g}$ and $\text{Li}_{0.3}\text{MnO}_2$, LOT 1003 synthesized from them with SSA $30 \text{ m}^2/\text{g}$.

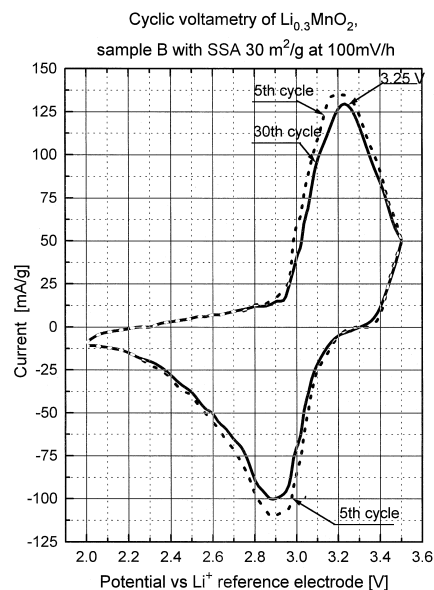


Fig. 2. Cyclic voltammogram of $\text{Li}_{0.3}\text{MnO}_2$ at the 5th and 30th cycle.

depending on the synthesis conditions. The X-ray diagrams are absolutely identical, thus, only the second one of the product with high SSA is shown. Fig. 1 also shows that the initial structure is well preserved. To check the reversibility of thus synthesized electrode material a slow cyclic voltammetry was applied. In Fig. 2 are presented the 5th and the 30th cycles of $\text{Li}_{0.3}\text{MnO}_2$ with $30 \text{ m}^2/\text{g}$. It can be seen that the charge and the discharge curves are similar to each other thus demonstrating very high reversibility of the material. After 30 cycles the charging potential is shifted only by 50 mV to higher values. A small reduction of the discharge capacity of about 15% from the starting one is observed also.

Test electrodes with sample A (SSA $10 \text{ m}^2/\text{g}$) and B (SSA $30 \text{ m}^2/\text{g}$) have been subjected to long cycling tests at different current drains. Fig. 3 represents the results from the tests. It is demonstrated that the specific capacity depends on the applied current drains, but not as much as expected from previous data [2,3,5]. The main idea of the work was to try to find correlation between delivered capacity and SSA, as we find in primary manganese dioxides and their reversibility when they are used in secondary cells. The result presented in Fig. 3 shows only 10–20% larger capacity when the SSA is almost tripled. If the specific current load by area is the basis of comparison the difference is more pronounced (Fig. 4). The dependence is presented in Fig. 4 showing the utilization of the reversible capacity on the current load.

The long time cycling of samples with SSA $30 \text{ m}^2/\text{g}$ at different charge discharge rates is presented on Fig. 5. It is demonstrated that the sample with high SSA exhibits very attractive electrochemical behavior and characteristics at high current drains. The sample delivers about 85% at C/8, 75% at C/4 and more than 65% at C/3 which up to

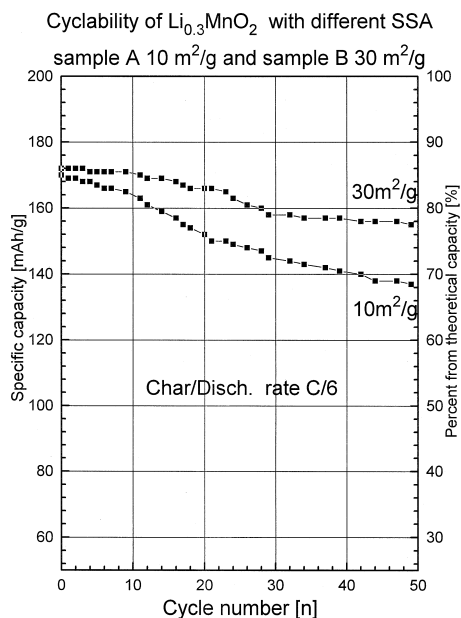


Fig. 3. Cyclability of $\text{Li}_{0.3}\text{MnO}_2$ with different SSA, 10 and 30 m^2/g at C/6 charge-discharge rate.

now was reserved only for LiMn_2O_4 . Fig. 6 represent the utilization of the theoretical electrode material capacity on the applied current loads, depending also on the cycle number. It can be seen from the picture that even at rates as high as 1 C the $\text{Li}_{0.3}\text{MnO}_2$ delivered more then 55% from its theoretical capacity and only after 40 cycles the reversible capacity is below 40%.

The comparison of different cathode materials at relatively moderate charge discharge rates is demonstrated in

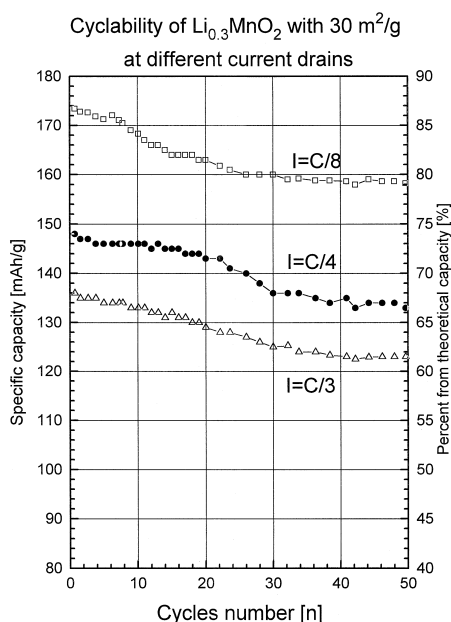


Fig. 4. Discharge capabilities of $\text{Li}_{0.3}\text{MnO}_2$ at different current loads.

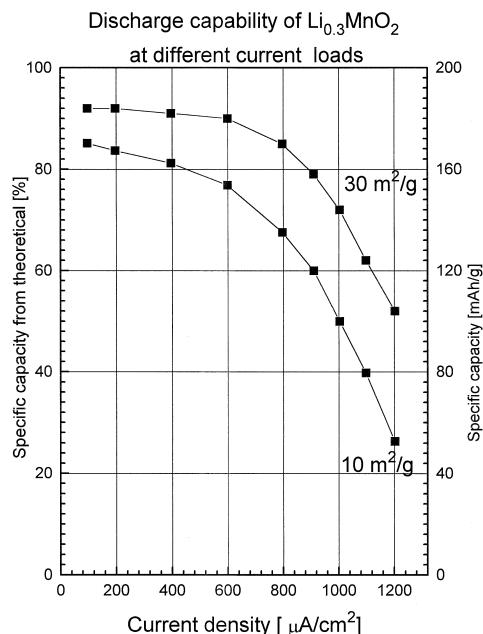


Fig. 5. Reversible capacity and cyclability of $\text{Li}_{0.3}\text{MnO}_2$ at different charge-discharge currents.

Fig. 7. The tested samples were: $\text{Li}_{0.3}\text{MnO}_2$ with SSA of 30 m^2/g , Faradizer M, specially treated (est.), and new standard JEC sample No. 1 of lithiated manganese dioxide, $\text{Li}_{0.3}\text{MnO}_2$ of the same type [9]. All test electrodes have been prepared in the same way [3–5] to avoid all deference. The electrochemical tests have been carried out in a laboratory test cell with limited electrolyte volume and Li reference electrodes. The dimensions of the test electrodes are exactly the same as for CR2032 cell. It is demonstrated that the optimized $\text{Li}_{0.3}\text{MnO}_2$ cathode material exhibits very attractive electrochemical behavior than the standard

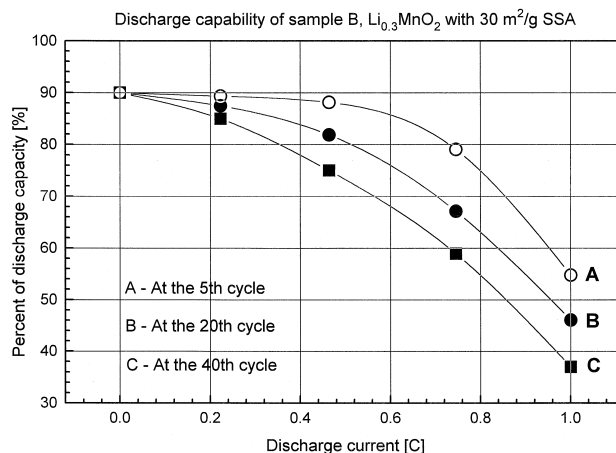


Fig. 6. Capacity dependence on the current drains of $\text{Li}_{0.3}\text{MnO}_2$.

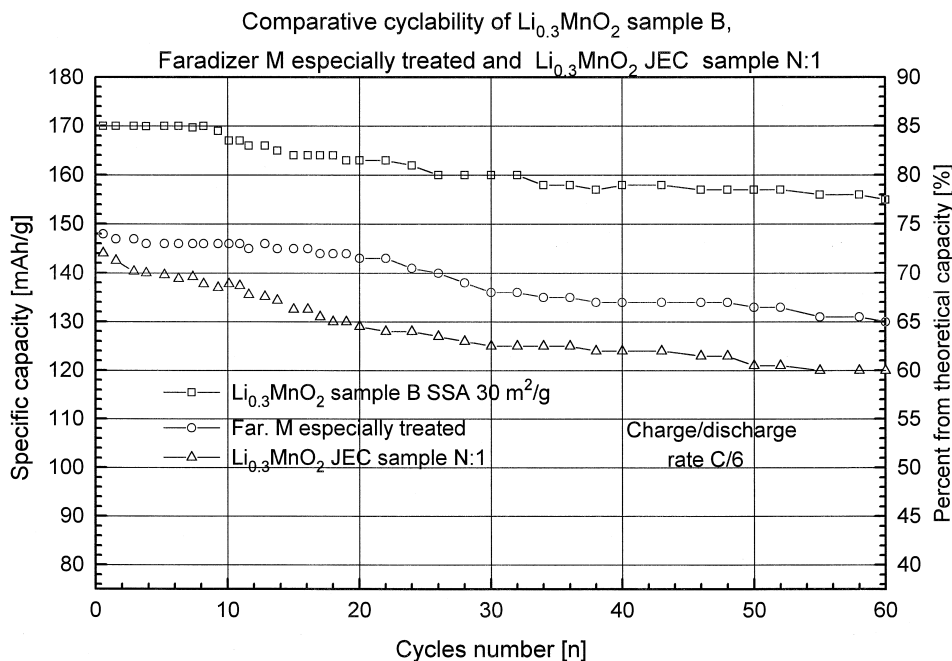


Fig. 7. Comparative diagram of $\text{Li}_{0.3}\text{MnO}_2$ sample B (SSA 30 m²/g), Faradizer M (specially treated) and $\text{Li}_{0.3}\text{MnO}_2$ JEC sample No. 1.

JEC sample No. 1. According to our previous papers [2,3,5] we show again that CMD Faradizer M can become the most prospective precursor for preparing secondary cathode material.

4. Conclusions

The reversible capacity and stability on cycling of sample B (with SSA 30 m²/g) are also higher than that of the sample with lower SSA. An initial capacity of 170 mAh/g within the first 10 cycles and more than 140 mAh/g at the 100th cycle at C/6 were obtained when the current density does not exceed 0.75 mA/cm². When a C/3 hour charge/discharge rate was applied, 160 mAh/g was obtained at the 20th cycle and about 130 mAh/g at the 100th cycle. The capacity retention is more than 90% for a period of 3 months without any cyclability deteriora-

tion. A coin lithium-ion cell, CR2032, has been assembled with specific energy density of 400 mWh/g for more than 50 cycles, assumed to the pure active cathode material.

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