

LiMn₂O₄ for 4 V lithium-ion batteries

V. Manev, B. Banov *, A. Momchilov, A. Nassalevska

Central Laboratory of Electrochemical Power Sources, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

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Abstract

LiMn₂O₄ spinel samples, synthesized by the reaction of Li₂CO₃ and MnCO₃ in air in several steps, have been evaluated as the electrode materials in 4 V lithium-ion cells. It was shown that the synthesis in the temperature range 500–750 °C leads to compounds with very poor electrochemical behavior. This is explained by a model of the chemistry of LiMn₂O₄ preparation proposed by Howard. On the basis of this model a new scheme of LiMn₂O₄ preparation is proposed. It was established experimentally that compounds with very high electrochemical characteristics can be obtained by a stepwise synthesis process, proceeding at three narrow temperature intervals.

Keywords: Lithium-ion batteries; Lithium; Manganese dioxide

1. Introduction

From the point of view of starting materials, price, and toxicity LiMn₂O₄ has a considerable advantage over LiNiO₂ and LiCoO₂, for its use as electrode material, and this makes LiMn₂O₄ an exceptionally promising compound for Li-ion batteries. In a recent series of papers [1–3] we have demonstrated that the preparation of LiMn₂O₄ spinel with high electrochemical performance depends on many parameters that render the synthesis a rather complex procedure. In spite of these obstacles, using chemical MnO₂ (CMD) and LiNO₃ as the starting materials, we have proved that it is possible to obtain a product, which is capable of exchanging reversibly 0.9 equivalents of Li at a 3 h rate [1–3]. However, the use of LiNO₃ for the industrial preparation of LiMn₂O₄ entails substantial pollution problems, related to the NO₂ evolution. The considerable water content in commercial MnO₂ [4], which can vary with the prevailing relative humidity, and the substantial variation in the Mn valency in commercial MnO₂ products complicated the precise evaluation of the Li/Mn ratio in the reaction mixture. In our previous paper [3], we have demonstrated that the starting Li/Mn ratio has a significant impact on both the specific capacity and the cycleability of the final product. This consideration leads to the conclusion that, in spite of the fact that CMD and LiNO₃ are the best starting materials for the production of LiMn₂O₄ on laboratory scale, they are extremely unsuitable for commercial production of LiMn₂O₄ for 4 V secondary lithium batteries.

In this work we consider the possibility of preparation of high performance LiMn₂O₄ spinel for 4 V lithium-ion batteries by using MnCO₃ and Li₂CO₃ or MnO₂ and Li₂CO₃ as the starting materials.

2. Experimental

The lithium salts used were Li₂CO₃ and LiClO₄, produced by Chemetall GmbH, MnCO₃ was manufactured by the Devnya Plant, Bulgaria, and MnO₂ was CMD Faradizer M supplied by Sedema. LiMn₂O₄ spinel was prepared by using appropriate amounts of MnCO₃ and Li₂CO₃ or MnO₂ and Li₂CO₃. The composite test electrode material was a mixture of the compounds studied and Teflonized acetylene black (TAB-2) at 1:1 ratio by weight. The electrochemical measurements were performed in a three-electrode glass cell with EC:DMC/LiClO₄ as the electrolyte.

Electron micrography was performed by JEOL 200-CX. The integral pore-size distribution curves were obtained by Micrometric-Auto Pore 9200.

3. Results and discussion

In our preliminary attempts to replace LiNO₃ with Li₂CO₃ in the LiMn₂O₄ synthesis from MnO₂ we used a long-term precursory heat treatment of the reaction mixture in the range of 500–550 °C which was proved previously to be very useful in the synthesis of LiMn₂O₄ from LiNO₃ and MnO₂. The

* Corresponding author.

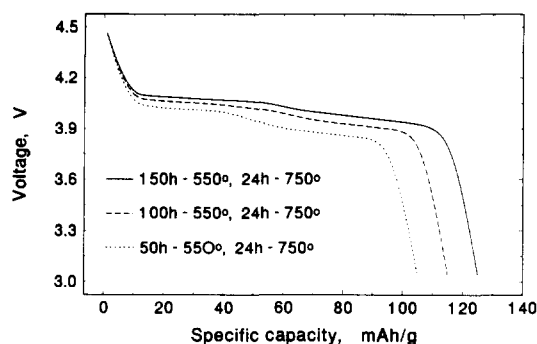


Fig. 1. Effect of pre-treatment time at 550 °C on the specific capacity of LiMn_2O_4 prepared from MnO_2 and Li_2CO_3 at 750 °C ($I_{\text{ch}} = I_{\text{deh}} = 0.3 \text{ C}$).

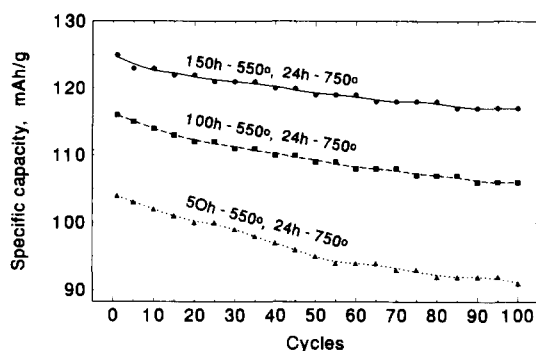


Fig. 2. Influence of pre-treatment time at 550 °C on the cycling performance at 3 h charge/discharge rate of LiMn_2O_4 prepared from MnO_2 and Li_2CO_3 at 750 °C.

discharge curves at a 3 h rate of a test electrode of LiMn_2O_4 , obtained from a mixture of MnO_2 and Li_2CO_3 , pre-treated at 550 °C for periods from 50 to 150 h and subsequently synthesized for 24 h at 750 °C, are presented in Fig. 1. It is seen that the specific capacity of the samples prepared from MnO_2 and Li_2CO_3 rises with the preliminary treatment time at 550 °C. The samples preliminary treated at 550 °C during 150 h possess a specific capacity of 125 mAh/g which is a comparatively good result but lower than that of the samples obtained from LiNO_3 [1–3]. It was established that the cycling behaviour of the LiMn_2O_4 electrodes depends significantly on the pre-treatment time at 550 °C. This is illustrated in Fig. 2 showing the decay of the specific capacity of LiMn_2O_4 electrodes obtained from a mixture of MnO_2 and Li_2CO_3 with the number of cycles.

The results obtained with LiMn_2O_4 samples directly synthesized from Li_2CO_3 and MnCO_3 using the same standard technique were very discouraging. This is illustrated in Fig. 3 that gives the discharge curves at 3 h charge/discharge rate of test electrodes consisting of LiMn_2O_4 samples synthesized from Li_2CO_3 and MnCO_3 with different initial specific surface areas. The samples were pre-heated at 550 °C for 50 h and then treated at 750 °C for 24 h. Obviously, the specific capacity increases with the initial specific surface area of MnCO_3 , reaching a maximum of 114 mAh/g, equal to 0.77 of the theoretical value. The results of the long-term cycling test of LiMn_2O_4 electrodes synthesized from Li_2CO_3 and

MnCO_3 with different initial specific surface areas are shown in Fig. 4. It can be concluded from Figs. 3 and 4 that the samples synthesized from MnCO_3 with a higher specific surface area not only display higher specific capacity but a better reversibility as well. However, considering the data reported in Refs. [2,3], the results presented in Figs. 3 and 4 are rather unsatisfactory.

As illustrated in Fig. 5, the increase in duration of the pre-heating at 550 °C from 50 to 150 h has no impact on the specific capacity or on the cycleability of the final product. This suggests that, in the case of using Li_2CO_3 and MnCO_3 as the starting materials, intermediate stable products are obtained during the first 50 h heating period at 550 °C. At the same time, one can conclude from this figure that the sample pre-treated at 450 °C has unexpectedly better electrochemical

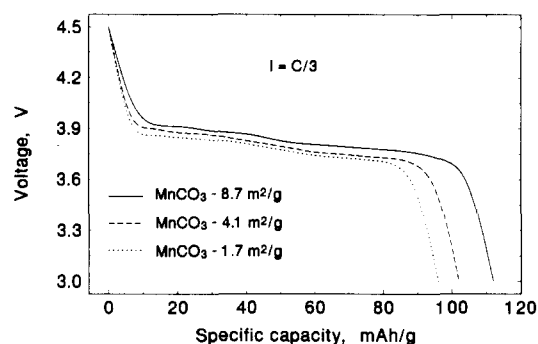


Fig. 3. Discharge curves at $I = 0.3 \text{ C}$ of LiMn_2O_4 synthesized from Li_2CO_3 and MnCO_3 with different initial specific surface areas.

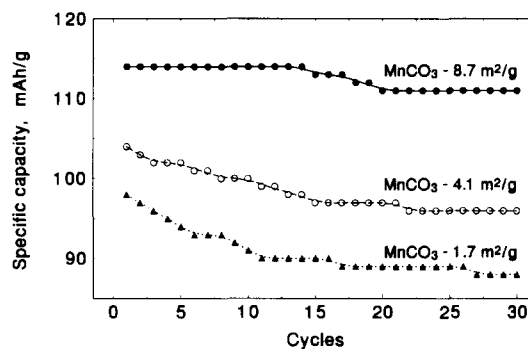


Fig. 4. Specific capacity vs. cycle number at $I = 0.3 \text{ C}$ for LiMn_2O_4 synthesized from Li_2CO_3 and MnCO_3 with different initial specific surface areas.

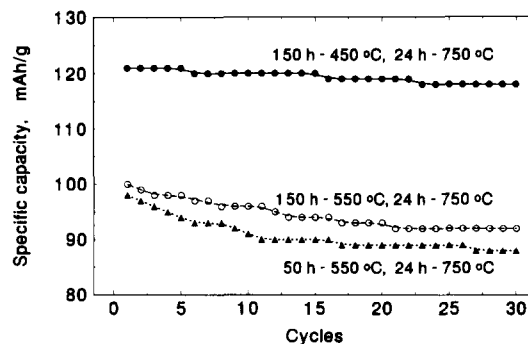
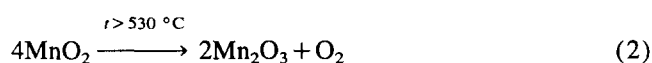
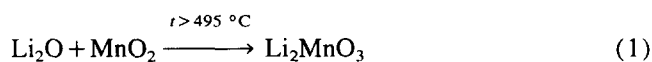


Fig. 5. Specific capacity vs. cycle number ($I = 0.3 \text{ C}$) of LiMn_2O_4 , from MnCO_3 with specific surface area $1.7 \text{ m}^2/\text{g}$ and Li_2CO_3 , prepared at different thermal conditions.

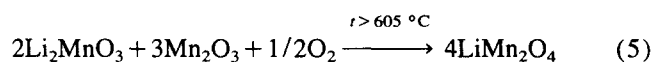
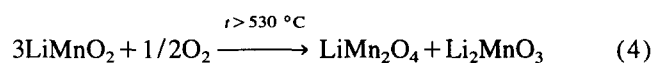
performance than the samples pretreated at 550 °C. This is an indication that, depending on the temperature, during the synthesis of the LiMn_2O_4 different intermediate compounds can be obtained, which have a significant effect on the electrochemical performance of the final product. These results led us to consider all possible reactions that could proceed during the LiMn_2O_4 synthesis; on the basis of this information a better method for the LiMn_2O_4 spinel preparation could be determined.

According to Howard [5,6], who has made a very detailed study on the chemistry of the LiMn_2O_4 formation from Li_2O and MnO_2 , the first main step is associated with three chemical reactions:



It is very important to note that these three chemical reactions lead to the formation of three intermediate products: LiMnO_2 , Mn_2O_3 and Li_2MnO_3 , which are electrochemically inactive in the 4 V range versus Li/Li^+ .

According to Howard [5,6], the second main step is actually associated with two iterative reactions as follows:

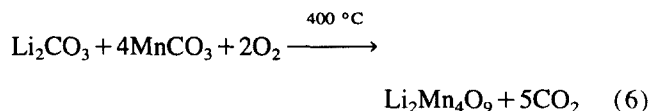


It is evident that reaction (4) cannot proceed if, for example, the orthorhombic phase LiMnO_2 is covered by preliminary nucleated spinel LiMn_2O_4 and by the rock-salt phase Li_2MnO_3 whereby the access of O_2 to the orthorhombic phase will be strongly hindered. Note that LiMnO_2 is thermodynamically stable in the 500–1000 °C temperature range in an inert atmosphere [7]. Similarly, reaction (5) cannot proceed if the rock-salt phase Li_2MnO_3 is separated from the Mn_2O_3 grains by LiMn_2O_4 preliminary nucleated between them, because the two phases (Li_2MnO_3 and Mn_2O_3) are thermodynamically stable in the 500–750 °C temperature range [8], usually applied for the preparation of the LiMn_2O_4 spinel [1–6]. Obviously the last two reactions (4) and (5) have the tendency to autoblock themselves, and this can be a source of considerable impurities in the final product.

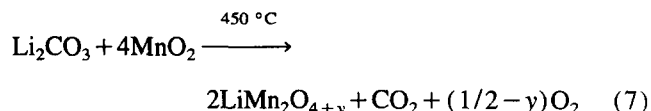
These examples can give an explanation why the solid-state reactions for the LiMn_2O_4 preparation, from Li_2CO_3 and MnCO_3 in the 500–750 °C temperature range, lead to a product with a specific capacity much lower than that of the theoretical value (148 mAh/g). It seems that in this case a certain amount of intermediate and simultaneously inactive compounds, namely LiMnO_2 , Li_2MnO_3 and Mn_2O_3 , can remain in the final product. The fact that they cannot be detected by X-ray diffraction analysis is probably due to the small crystal grain size of these impurities. At the same time,

these considerations lead to the conclusion that the history of the thermal and mechanical treatment of the reaction mixture can have a great impact on the electrochemical behaviour of the synthesized LiMn_2O_4 spinel.

Fortunately the scheme, shown by Howard [5,6], is not the only one which can proceed during the LiMn_2O_4 spinel preparation. The synthesis of LiMn_2O_4 can be performed by eliminating of intermediate inactive compounds of LiMnO_2 , Li_2MnO_3 and Mn_2O_3 . As was shown by Thackeray and co-workers [8,9] the reaction between Li_2CO_3 and MnCO_3 at 400 °C leads to the synthesis of a high oxygen content spinel $\text{Li}_2\text{Mn}_4\text{O}_9$ by the reaction:



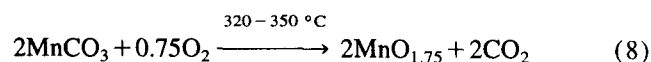
According to our own data the reaction between lithium salts and MnO_2 at 450 °C leads to a high oxygen content distorted spinel [1,2] with a stoichiometry $\text{LiMn}_2\text{O}_{4+y}$ by the following reaction:



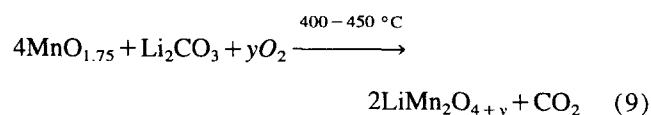
where y has an approximate value of 0.15. As can be concluded from Eqs. (6) and (7) a temperature window exists between 400 and 450 °C where a high oxygen content distorted spinel can be synthesized without nucleation of any of the inactive intermediate products. As a last step of this scheme, the stoichiometric spinel LiMn_2O_4 can be obtained from this precursor just by heating at 750 °C for 24 h.

It is evident from the data presented on Figs. 1–4 that the use of MnO_2 and Li_2CO_3 instead of MnCO_3 with Li_2CO_3 for the synthesis of the LiMn_2O_4 spinel has a beneficial effect on the electrochemical performance of the final product. The disadvantage of using MnCO_3 can be overcome by preliminary heating at 350 °C in air, which, according to Welsh and Picquet [10], leads to a non-stoichiometric MnO_2 with an oxidation state approximately equal to $\text{MnO}_{1.75}$ – $\text{MnO}_{1.8}$. Using this as a first step, a three-step synthesis of LiMn_2O_4 from MnCO_3 and Li_2CO_3 can be performed by avoiding the scheme described by Howard [5,6], as follows:

(i) first step:

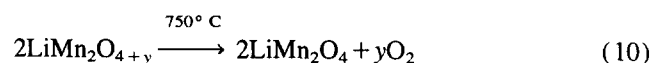


(ii) second step:



where y is in the range $0.15 < y < 0.5$.

(iii) third step:



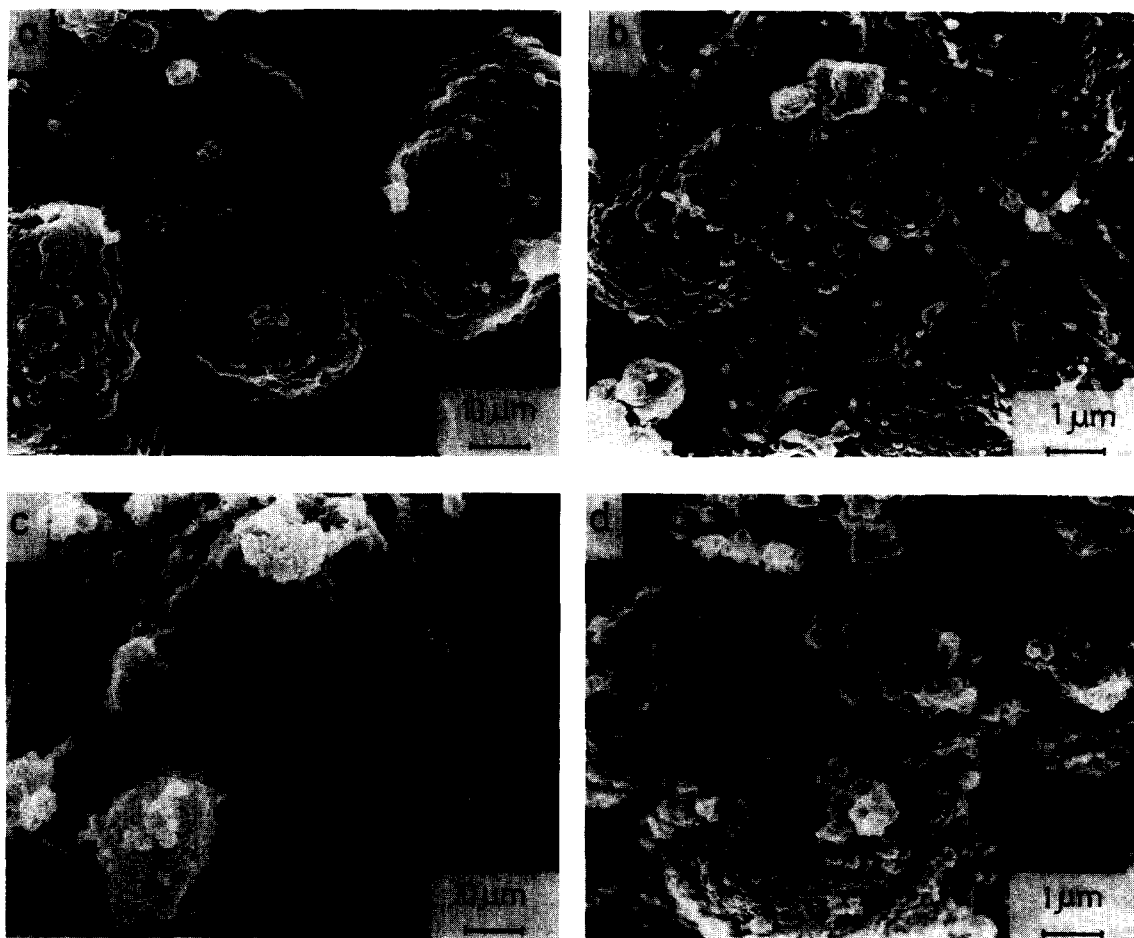


Fig. 6. SEM pictures (a) and (b) of the precursor $\text{MnO}_{1.75}$ and (c) and (d) of the LiMn_2O_4 after the last step, prepared according to the scheme described by Eqs. (8)–(10).

The second step is associated with the mass transport of the lithium salt into the manganese oxide which requires much longer reaction time than the other two steps. Scanning electron microscopy (SEM) pictures of the samples after the first step (Fig. 6(a) and (b)) and after the last step (Fig. 6(c) and (d)) confirm the need of a long reaction time for the second step described by Eq. (9). It can be seen in Fig. 6(a) and (b) that the typical morphology of the precursor $\text{MnO}_{1.75}$ are particles with a mean diameter of about $50 \text{ m}\mu$.

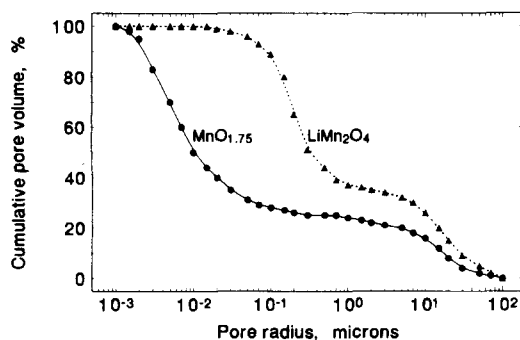


Fig. 7. Cumulative pore-size distribution curves of the precursor $\text{MnO}_{1.75}$ and LiMn_2O_4 prepared according to the scheme described by Eqs. (8)–(10).

It is evident that the penetration of the Li_2O into these particles by a solid-state reaction will require at least several days, because, after the synthesis of the final product LiMn_2O_4 (Figs. 6(c) and (d)), the macro-morphology is not much affected, and a tendency for the particles to grow can even be observed (Fig. 6(a) and (c)).

In the high magnification SEM pictures (Fig. 6(b) and (d)) one cannot distinguish very well the precursor $\text{MnO}_{1.75}$ microstructure from that of the final product LiMn_2O_4 . However, the integral pore distribution of these two compounds shown in Fig. 7 reveals that the mean micropore radius of the precursor (about 80 \AA) is by more than one order of magnitude lower than that of the synthesized LiMn_2O_4 spinel (about $0.2 \text{ m}\mu$).

The electrochemical behaviour of the compounds prepared from MnCO_3 and Li_2CO_3 by the scheme described by Eqs. (8)–(10) is given in the next two figures. Fig. 8 shows the charge/discharge curves in the second cycles of LiMn_2O_4 electrodes at the 3 h rate ($I = 0.3 \text{ C}$) and 0.5 h rate ($I = 2 \text{ C}$). It is evident from Fig. 8, that the initial specific capacity at 3 h charge/discharge rates is about 130 mAh/g , while at the exceptionally fast charge/discharge rate of $I = 2 \text{ C}$ the specific capacity decrease is less than 10% and is still about 120

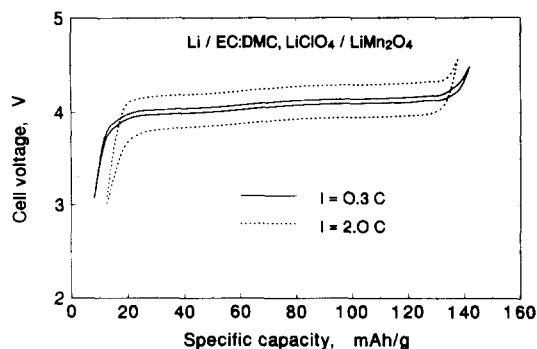


Fig. 8. Second cycle charge/discharge curves of LiMn_2O_4 test electrodes from MnCO_3 and Li_2CO_3 , synthesized according to the scheme described by Eqs. (8)–(10).

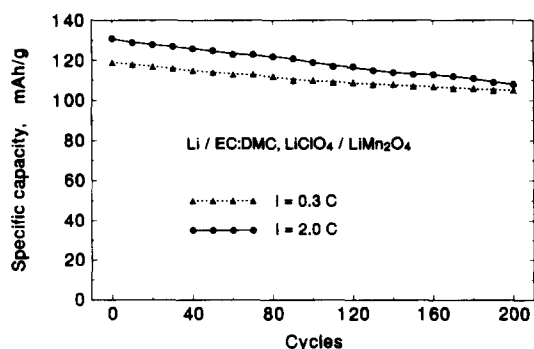


Fig. 9. Specific capacity vs. cycle number of LiMn_2O_4 test electrodes from MnCO_3 and Li_2CO_3 , synthesized according to the scheme described by Eqs. (8)–(10).

mAh/g . Fig. 8 presents the unique feature of the LiMn_2O_4 spinel to withstand extremely high charge/discharge rates without any substantial increase in electrode polarization and specific capacity loss.

The results of the long-term cycling of the LiMn_2O_4 test electrodes, synthesized from MnCO_3 and Li_2CO_3 by the scheme described by Eqs. (8)–(10) at 3 h charge/discharge rate ($I=0.3\text{ C}$) and 0.5 h rate ($I=2\text{ C}$) are shown in Fig. 9. Unexpectedly, the cycleability of the LiMn_2O_4 electrode at higher charge/discharge rate ($I=2\text{ C}$) is better than that of the comparatively lower one ($I=0.3\text{ C}$). This result can be explained by the fact that at higher charge/discharge cycling rate, the amount of the Li ion exchange is lower and this leads to a more stable structure of LiMn_2O_4 during cycling in comparison with the lower cycling rate. The results displayed in Fig. 9 represent further evidence for the unique feature of LiMn_2O_4 to withstand unusually high charge/discharge rates during cycling.

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