THE EFFECT OF BALL MILLING AND TEMPERATURE TREATMENT ON THE ELECTROCHEMICAL PROPERTIES OF $LiMn_2O_4$ ELECTRODES

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ABSTRACT

In this paper we report on the preparation of positive electrodes for rechargeable lithium batteries, based on $LiMn_2O_4$. Two aspects are stressed. (i) The homogenization of the electrode mass (oxide, carbon, and binder) with a ball mill. For a good electric contact between oxide particles and carbon a milling time of 5 min is enough, as demonstrated by the low polarization of the electrode during cycling. After a longer period of milling, the specific capacity of the oxide decreases due to mechanical degradation of the oxide. (ii) The water content adsorbed at the surface of the electrode mass should be as small as possible. Therefore, a drying step is needed, but it can result in chemical reduction of $LiMn_2O_4$ by carbon if the temperature is higher than 175°C.

INTRODUCTION

Numerous papers have been published on the synthesis (1,2) of metal oxides with excellent properties for lithium-ion batteries, but it seems still to be difficult to make good composite electrodes from the oxides and the necessary additives like carbon and binder. The capacity fading during electrode cycling and its mechanism is an important problem (3,4). Many problems are caused by the electrode preparation process itself. In this paper we investigate the mechanical and thermal treatment of $LiMn_2O_4$-based electrode masses and its effects on the electrochemical performance of electrodes prepared from these masses.

Mechanical effects like partly disintegration of sintered grains of primary oxide particles are observed during the homogenization of the components of the active mass if a ball mill is used for this operational step. On the one hand the carbon for the electric conductivity consists of spherical agglomerates which should be grinded, on the other hand neither the sintered grains nor the primary oxide particles should be modified during the homogenization.

Furthermore, the temperature treatment is important because the electrode mass has to be dried rigorously to achieve good cycle stability in the electrochemical experiment. A treatment at a temperature higher than 100°C is needed to keep the drying time short. On the other hand the temperature cannot be too high because a chemical reaction between the oxide and carbon may take place.

For both electrode preparation steps a compromise has to be found to get good results in the electrochemical behavior of the electrodes and finally of the whole cell. How such compromises look like for practical needs is described in the following sections.

EXPERIMENTAL

A ball mill container with balls, both made of ZrO_2, was used for the wet mixing of 250 mg $LiMn_2O_4$ (12 batches, BASF/EMTEC), 250 mg carbon (e.g., Vulcan XC-72), and 10 mg polytetrafluoroethylene (PTFE) powder as organic binder (Teflon® MP 1000, Du Pont) in hexane (Fluka, for HPLC, > 95%) for 120 min and 5 min in the long and short time case, respectively. After the milled slurry was dried and homogenized, about 40 mg of the powder was pressed into a titanium current collector, resulting in about 300 µm thick electrodes with a geometrical area of 1.3 cm^2. The electrodes were then dried in vacuum at 100 - 225°C for 12 h before the cells were assembled in an argon-filled glove box.

All electrochemical experiments were performed in laboratory cells (5), with Li (Aldrich, 99.9%, 0.75 mm thickness) metal as counter and reference electrode, and using a solution of 1M $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1:1) from Merck (battery electrolyte liquid LP30, Selectipur®) as an electrolyte. We used a current density of 10 $\mu A/mg_{oxide}$ for the galvanostatic cycling experiments in the potential range from 3.3 to 4.4 V vs. Li/Li^+. The measured specific charges are always given with respect to the $LiMn_2O_4$ in the electrodes only.

Scanning electron microscopy (SEM) characterization was done with a Topcon ABT-60 instrument using 10 kV acceleration voltage. The specific surface area measurement (Brunauer-Emmett-Teller, BET) was performed as follows: The powder was dried at 140°C for at least 12 hours. The specific surface area was measured with a Ströhlein sorptometer using the single-point-difference method according to Haul and Dümbgen (6).

RESULTS AND DISCUSSION

Effect of Ball Milling

We observed that the milling time used to produce a slurry of $LiMn_2O_4$, carbon, and PTFE strongly influences the electrochemical performance of the electrode mass. To understand the influence of ball milling we studied the milling of the pure oxide separately. The wet milling of $LiMn_2O_4$ results in an increased BET specific surface area of the oxide (7) (Fig. 1). After two hours of milling the specific surface area is about 4 times higher than that of the starting material. Further milling for periods of time of up to 14 hours results in an insignificant increase in the BET specific surface area. That means that the main change of the BET specific surface area is caused within 2h of milling.

The comparison of the SEM images of the starting oxide material (Fig. 2) and of the sample after 14 h of milling (Fig. 3) shows that the primary oxide particles are approximately of the same size. That means that the difference in the specific surface area is related to a higher level of the hierarchic structure of the powder materials. It may be caused by breaks of sintered grains of primary oxide particles creating new surfaces without change of the size of the primary particles. Another contribution comes probably from the fine dust that is unavoidable produced by the abrasive process of ball milling. For our further discussion we assume that a change in surface area after 5 min of milling could be neglected.

The milling process of the slurry of the electrode components significantly influences the electrochemical properties of the $LiMn_2O_4$ based active mass. After 120 min of milling the specific charge of the oxide is about 10 % lower than after 5 min (Fig. 4). The shape of the charge/discharge curves of a $LiMn_2O_4$ electrode changes from the typical well-defined two plateaus for a spinel after 5 min milling to a less structured curve after 120 min milling (Fig. 5).

Furthermore, it follows from Fig. 5 that the polarization (8) of the electrode at a current density of 10 $\mu A/mg_{Oxide}$ is low (about ±10 mV for the de-insertion and insertion process) and hardly influenced by the milling time. A change in the capacity fading behavior during cycling (Fig. 4), was not observed.

We suggest that the change of the electrochemical behavior of the oxide as shown in Fig. 4 and Fig. 5 is induced by the mechanical stress during the milling process. In conclusion, the milling time should be as short as possible.

Effect of Heat Treatment

A chemical reduction of $LiMn_2O_4$ has been observed during heating of the electrode mass (oxide, carbon, and binder) at 200°C, which leads to the appearance of an additional 3 V-plateau on the first charge curve (Fig. 6, at the top). In our experiments this plateau is only observed in the first oxidation half-cycle, because the lower potential limit of the following cycling was fixed to 3.3 V vs. Li/Li^+, because only the specific charge and cyclability in the 4 V-region of the $LiMn_2O_4$-spinel-phase was of interest in our investigation. The reaction for the reversible lithium de-insertion/insertion at the 4 V-plateau can be described by the following reaction pattern:

$$LiMn_2O_4 \rightleftharpoons Li_{1-x}Mn_2O_4 + x\,Li^+ + x\,e^- \qquad [1]$$

Please note that the normal 3 V-plateau of the $LiMn_2O_4$ compound is still there and could be observed by lowering the potential, inducing the Li^+- insertion.

$$LiMn_2O_4 + Li^+ + e^- \longrightarrow 2\,LiMnO_2 \qquad [2]$$

The first cycle of a charge/discharge curve of an electrode dried at 100°C is shown in

Fig. 6, below. The open circuit voltage of the fresh cell is 3.17 V vs. Li/Li^+. After the current was switched on the potential reached a value typical for the beginning of the 4 V-plateau immediately.

The additional 3 V-plateau of the samples dried at 200°C must be due to the reaction of the oxide with carbon (reaction of $LiMn_2O_4$ with PTFE is less likely, moreover, only 2 % of binder are faced with a chemical reduction of the oxide of sometimes nearly 40%). This follows from the fact that no plateau is observed if the oxide is pre-heated at 200°C without carbon (Fig. 7, below) and then used to produce the homogeneous active mass by 5 min of ball milling and drying of the final electrodes at 100°C. The charge/discharge curve is exactly comparable to the curve measured for a electrode dried at 100°C (Fig. 7, at the top). The oxide reduction was observed for all tested carbon samples. A significant oxidation of the carbon by $LiMn_2O_4$ to CO or CO_2 could be excluded because the reaction occurs without detectable decrease in the weight of the reaction mixture. For the same reason a simple split-off of oxygen could be excluded, too.

It follows from Fig. 8 that the part of the $LiMn_2O_4$ that undergoes the chemical reduction with carbon during the drying is irreversibly lost for the reversible insertion/de-insertion of the Li^+ - ions in the 4 V-region. Therefore, the specific charge of the second and further cycles is lower. The reversible specific charge of a $LiMn_2O_4$/carbon electrode dried at 200°C reaches its highest value if no charge for the 3 V-plateau is observed. The data shown in Fig. 8 is taken from 12 different $LiMn_2O_4$ samples, but the same drying conditions. That means that the appearance and the extent of the 3 V-plateau depends strongly on the preparation of the $LiMn_2O_4$ samples*. Each $LiMn_2O_4$ sample has its own temperature sensitivity. Moreover, the charge loss increases with increasing time of the heat treatment. For example, at a temperature of 225°C samples have been dried for 12 h and 32 h. The specific charge at the 3 V-plateau in the first de-insertion step increased from 26.7 Ah/kg to 37.8 Ah/kg. Therefore the sample dried for 36 h showed a lower reversible charge/discharge behavior in the following cycles. The difference between the specific charge at the 3 V-plateau (11.1 Ah/kg) for samples dried for different time is about the same as the difference in charge of the following cycles between these samples (7.8 Ah/kg; 5th cycle).

To get more information about the chemical reaction between oxide and carbon we investigated the temperature dependence for a typical oxide sample. We discovered that a significant specific charge in the 3 V-region as a bulk property of the oxide is observed for temperatures higher than 175°C (Fig. 9). In summary, drying temperatures of > 175°C should be avoided but the optimal temperature must be determined for each particular $LiMn_2O_4$ type.

In the same analysis we noticed that the open circuit voltage of fresh cells as surface sensitive method is a practical test to detect exaggerated temperatures during electrode drying (Fig. 10). Its normal value is about 3.17 V vs. Li/Li^+ which comes down to about 2.95 V vs. Li/Li^+ for a treatment at 225 °C. The open circuit potential starts to decrease at temperatures higher than 125 °C.

* Please note that the stoichiometry and/or other relevant properties significantly vary for oxides generally described as $LiMn_2O_4$

CONCLUSIONS

(i) Ball milling of $LiMn_2O_4$ based electrode mass decreases the specific charge of the oxide due to the induced mechanical stress. (ii) The drying of a $LiMn_2O_4$/carbon mixture in vacuum should be carried out at temperatures lower than 200°C to avoid oxide reduction. The open circuit voltage of the cell can be used to determine if the heat treatment was carried out properly.

ACKNOWLEDGMENTS

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FIGURES

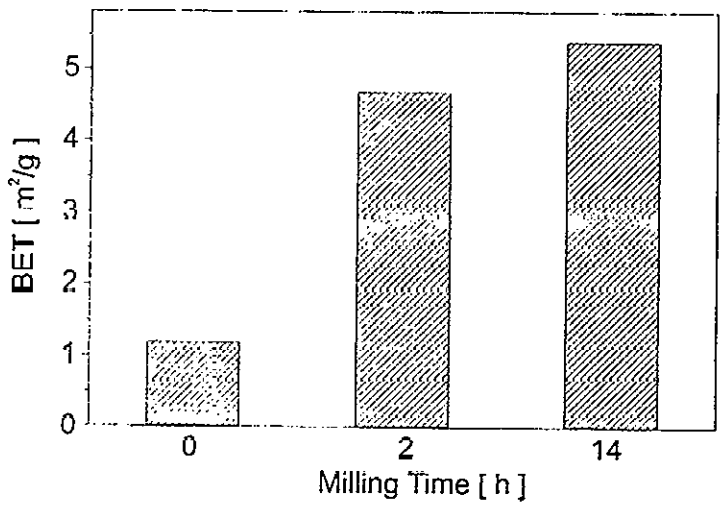

Fig. 1 Dependence of the BET specific surface area of $LiMn_2O_4$ on the wet ball milling time.

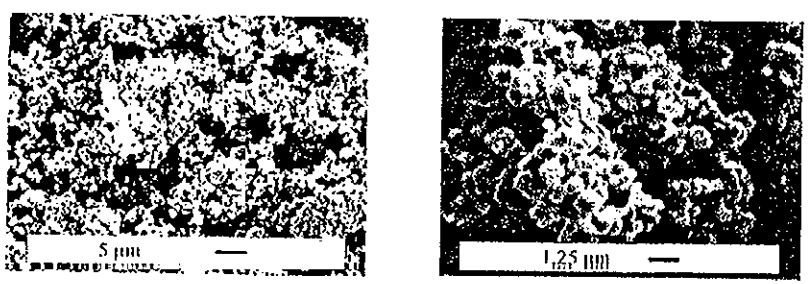

Fig. 2 SEM images of $LiMn_2O_4$ before milling.

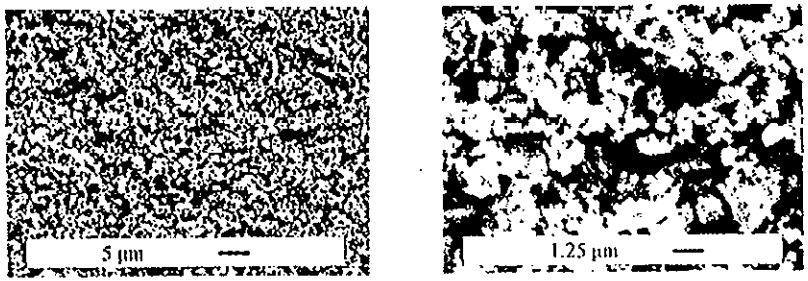

Fig. 3 SEM images of $LiMn_2O_4$ after 14 h of milling.

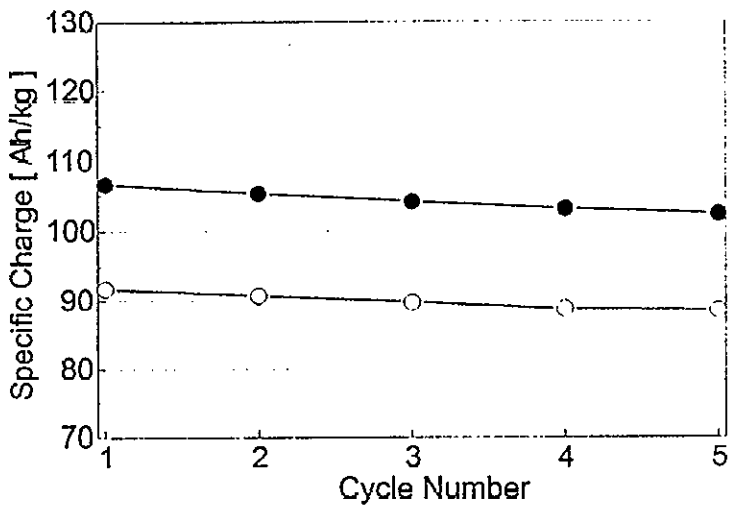

Fig. 4 The effect of ball milling of a $LiMn_2O_4$/carbon mixture for 5 min (—●—) and 120 min (—○—) on the specific charge of the oxide for lithium insertion.

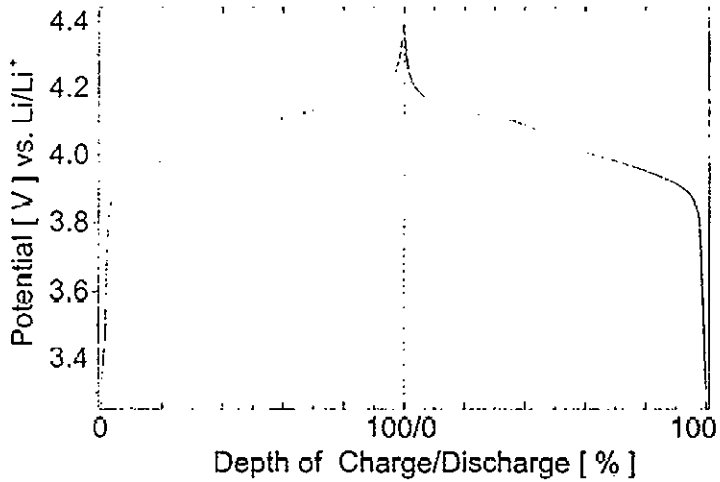

Fig. 5 The effect of ball milling of a $LiMn_2O_4$/carbon mixture for 5 min (—) and 120 min (• • •) on the shape of the galvanostatic charge/discharge curve (second cycle).

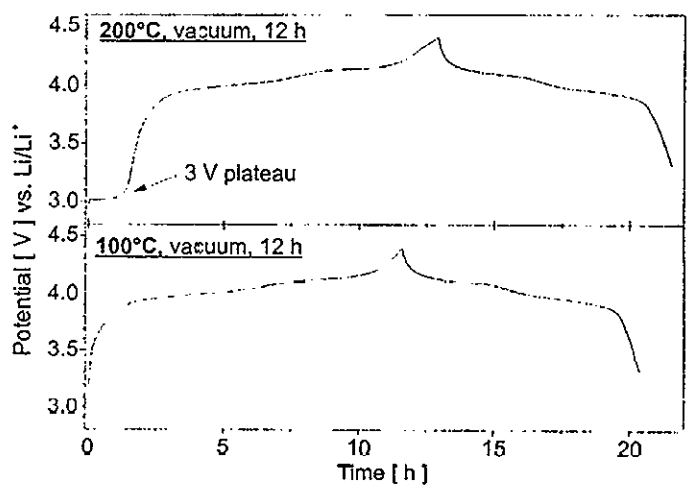

Fig. 6 Galvanostatic charge/discharge curves of $LiMn_2O_4$/carbon electrodes dried at 100 and 200°C. Note the plateau at about 3 V vs. Li/Li^+ for the sample dried at 200°C.

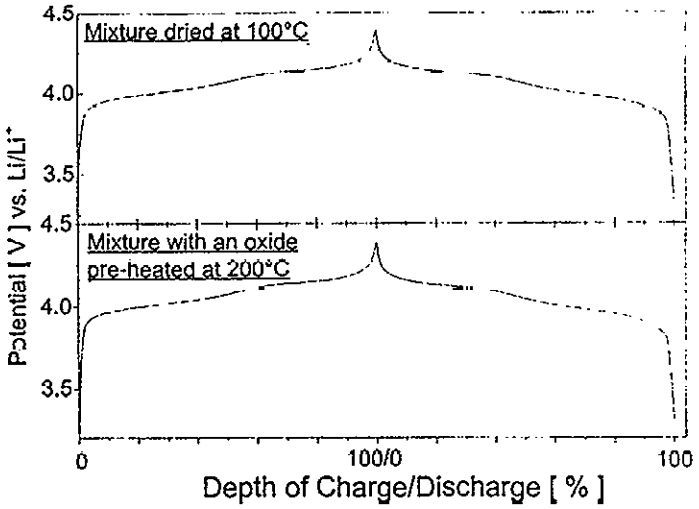

Fig. 7 Galvanostatic charge/discharge curves of $LiMn_2O_4$/carbon electrodes dried at 100°C. The oxide of the lower curve was heat treated at 200°C for 12h in vacuum before making the mixture.

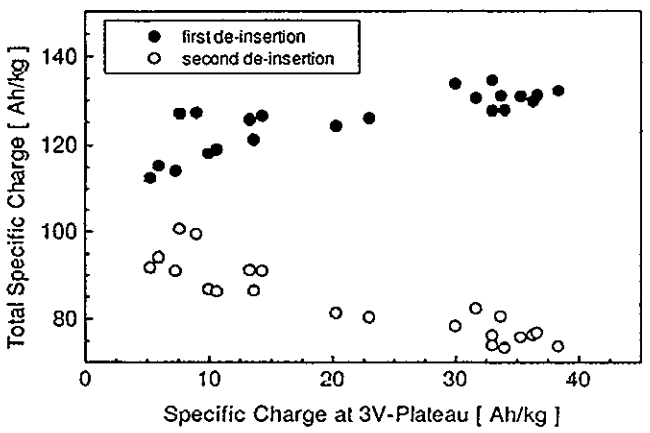

Fig. 8 Total specific charge for the 1st and 2nd cycle of lithium de-insertion from $LiMn_2O_4$/carbon electrodes dried for 12 h at 200°C as a function of the charge of the 3 V-plateau in the first Li^+-de-insertion. The data were obtained from 12 different $LiMn_2O_4$ samples.

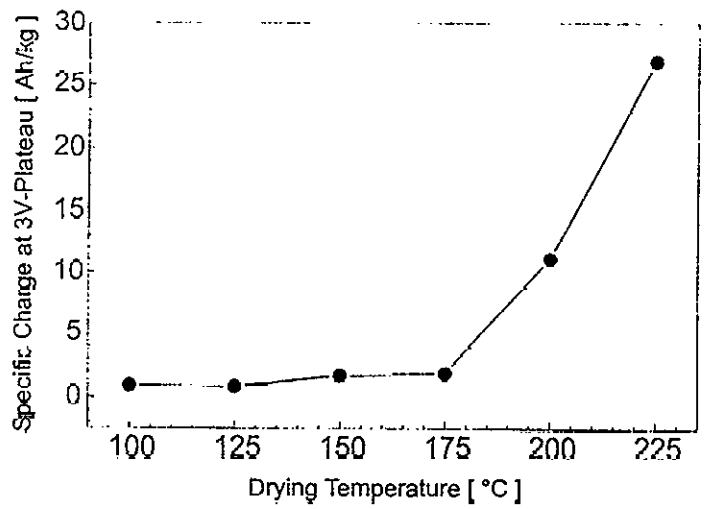

Fig. 9 Specific charge in the 3 V-region for the first lithium de-insertion from $LiMn_2O_4$/carbon electrodes dried at different temperatures.

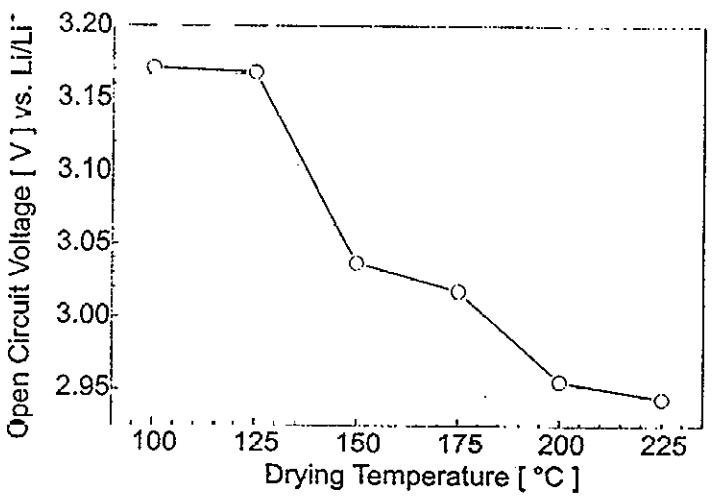

Fig. 10 Open circuit voltage measured against Li/Li^+ for $LiMn_2O_4$/carbon electrodes dried at different temperatures.

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