

LiMn₂O₄ cathode materials synthesized by the cellulose–citric acid method for lithium ion batteries

Peizhi Shen^a, Dianzeng Jia^{a,*}, Yudai Huang^a, Lang Liu^a, Zaiping Guo^b

^a Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, PR China

^b Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, NSW 2522, Australia

Received 15 May 2005; received in revised form 28 September 2005; accepted 29 September 2005

Available online 17 November 2005

Abstract

A new technique was employed to synthesize spinel LiMn₂O₄ cathode materials by adding cellulose and citric acid to an aqueous solution of lithium and manganese salts. Various synthesis conditions such as the calcination temperature and the citric acid-to-metal ion molar ratio (*R*) were investigated to determine the ideal conditions for preparing LiMn₂O₄ with the best electrochemical characteristics. The optimal synthesis conditions were found to be *R* = 1/3 and a calcination temperature of 800 °C. The initial discharge capacity of the material synthesized using the optimal conditions was 134 mAh g⁻¹, and the discharge capacity after 40 cycles was 125 mAh g⁻¹, at a current density of 0.15 mA cm⁻² between 3.0 and 4.35 V. Details of how the initial synthesis conditions affected the capacity and cycling performance of LiMn₂O₄ are discussed. © 2005 Elsevier B.V. All rights reserved.

Keywords: Lithium-ion battery; LiMn₂O₄; Citric acid; Cellulose

1. Introduction

The spinel LiMn₂O₄ has received a great deal of attention as the most promising cathode material for lithium secondary batteries because of its low cost and lower toxicity compared with the layered oxides LiCoO₂ and LiNiO₂ [1,2]. For commercial application, it is important to produce LiMn₂O₄ powders with excellent cyclability and high capacity at a relatively high current density. However, LiMn₂O₄ has problems related to capacity fading and limited cyclability in the 4 V region when compared to layered oxides. To solve these problems, many researchers have studied the mechanism of capacity fading and have suggested numerous solutions [3,4].

The quality of the LiMn₂O₄ powders strongly depends on the synthesis method and conditions. These conditions determine the physical and chemical properties of the materials, such as particle size, lattice parameters, stoichiometry and average Mn valence. In general, LiMn₂O₄ powders have been prepared by a solid-state reaction between mixed lithium and manganese

salts, followed by high-temperature calcination and extended grinding. This method has several disadvantages: inhomogeneity, irregular morphology, large average particle size with a broad particle size distribution, and poor control of stoichiometry. In recent years, “soft-chemical” methods have been widely used to synthesize the desired powders, such as sol–gel [5,6], the tartaric acid/citric acid gel process [7], the Pechini process [8], etc. In brief, the key point is how to prepare active materials with good performance by an easy and low cost method.

In this study, LiMn₂O₄ powders were synthesized by a new method that involves adding cellulose and citric acid to an aqueous solution of manganous acetate and lithium acetate. This synthesis method takes both the advantages of Pechini method (regular morphology and good electrochemical characteristics) and cellulose absorption method (inexpensive and simple). The powder characteristics and electrochemical performance were evaluated for varying sintering temperatures and citric acid-to-metal ion ratios.

2. Experimental

All reagents were analytically pure and were used without further purification. Experimental details are as follows.

* Corresponding author. Tel.: +86 991 8583265; fax: +86 991 8581006.
E-mail address: jdz@xju.edu.cn (D. Jia).

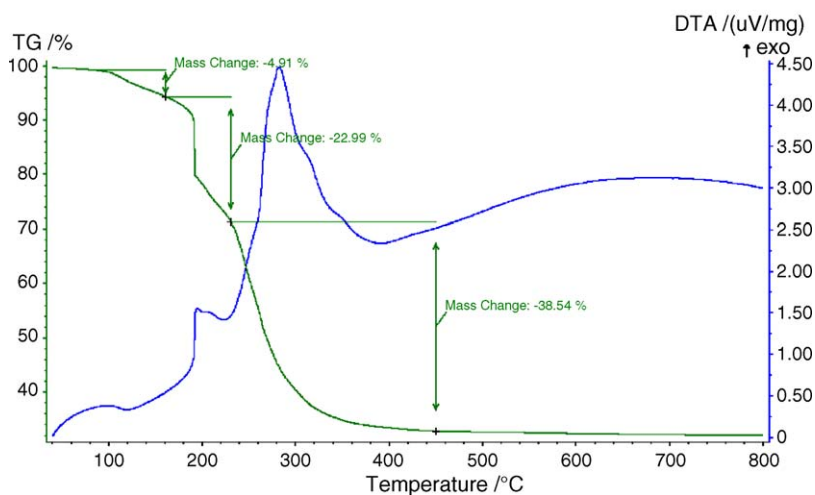


Fig. 1. Thermogravimetric and differential thermal curves of precursors at an air flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ and a heating rate of $10^\circ \text{C min}^{-1}$.

2.1. Synthesis of cellulose

A solution containing 5 mL concentrated HNO_3 and 10 mL concentrated H_2SO_4 was first prepared, then absorbent cotton was immersed and reacted in the solution for 20 min. The product obtained was washed with distilled water several times to remove the acid and by-products and then dried at room temperature.

2.2. LiMn_2O_4 preparation

0.01 mol lithium acetate and 0.02 mol manganous acetate were dissolved in distilled water. The prepared cellulose (0.6 g) was added to the aqueous solution and maintained at 50°C for 2 h. Then citric acid was added to the solution, which was held at 50°C for another 4 h. Different amounts of citric acid were added for different citric acid-to-metal ion molar ratios ($R = 1, 2/3, 1/3,$

$1/6,$ and $1/10,$ respectively). The mixture was then heated to 120°C to remove water, and a solid precursor was obtained. The precursor was decomposed at 450°C for 1 h to eliminate any organic content, ground slightly and then calcined in air at various temperatures ($550\text{--}900^\circ \text{C}$) for 10 h in a muffle furnace.

2.3. Characterization

The thermal decomposition behavior was examined by means of thermogravimetry (TG) and differential thermal analysis (DTA). An X-ray diffractometer with $\text{Cu K}\alpha$ radiation was used for the identification of the crystalline phases of the powders. The morphological characteristics of the product were examined by using scanning electron microscopy (SEM). A redox titration method using KMnO_4 as the titrant was used to measure the average valence of the manganese.

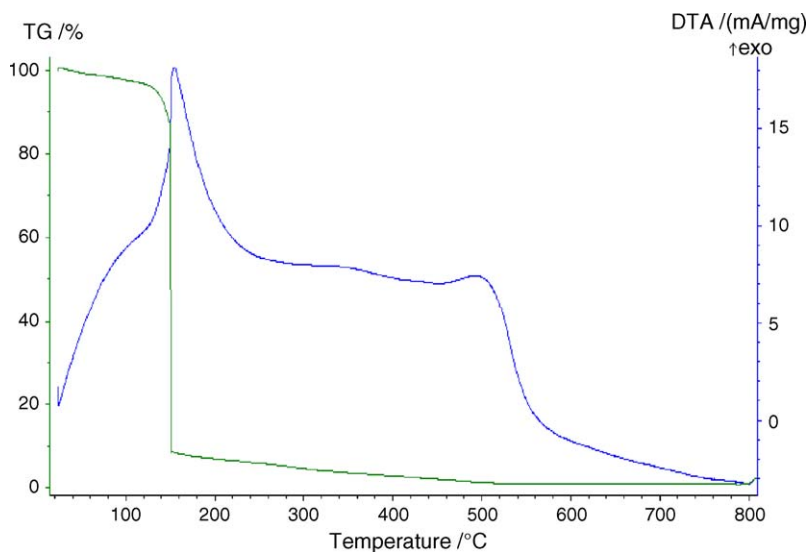


Fig. 2. Thermogravimetric and differential thermal curves of cellulose at an air flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ and a heating rate of $10^\circ \text{C min}^{-1}$.

2.4. Electrochemical measurements

The electrochemical cells consisted of an LiMn_2O_4 -based composite as the positive electrode, a Li disk as the negative electrode, and an electrolyte of 1 M LiPF_6 in a 1:1 (volume ratio) mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC). The cathode was made by mixing the active material with acetylene black and PVDF binder in an 85:10:5 ratio in *N*-methyl-pyrrolidone (NMP). NMP acts as the solvent for the binder. The paste was applied to aluminum foil current collectors using a blade. The film was dried at 60°C in air for 2 h in an oven and then was vacuum dried at 120°C for 3 h. The weight of the electrochemically active material was calculated from the total weight of the electrodes and the weight of the Al foil and additives. Celgard 2300 membrane was used as the separator. The cells were assembled in an argon-filled glove box. All the electrochemical tests were carried out at room temperature. Cyclic voltammetry (CV) experiments were conducted from 3.0 to 4.35 V at a scan rate of 0.1 mV s^{-1} , and a Li metal disk served as both counter and reference electrodes. Charge–discharge tests were performed at a constant current density of 0.15 mA cm^{-2} within the potential range of 3.0 to 4.35 V.

3. Results and discussion

Fig. 1 shows the TG and DTA curves of the precursor with $R=1$. There are three temperature intervals where significant mass loss can be detected. The first one is the interval between 80 and 160°C that corresponds to elimination of adsorption and intercalation water, as well as the main decomposition of cellulose. The decomposition of cellulose can be confirmed by the TG/DTA curves shown in Fig. 2. The second one is in the range between 160 and 230°C that corresponds to the decomposition of acetates. The third one in the temperature range 230 – 450°C

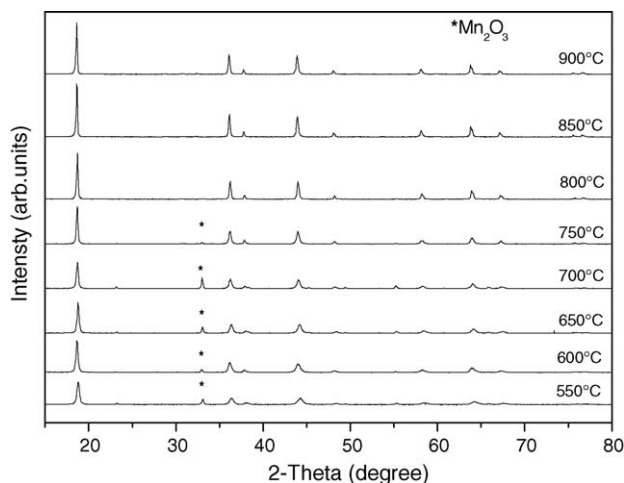


Fig. 3. XRD patterns of LiMn_2O_4 powders calcined at various temperatures with the molar ratio of citric acid to the total metal ions fired at 1.

can be considered as a result of the citric acid combustion and the crystallization of the spinel LiMn_2O_4 phase.

Fig. 3 shows XRD patterns for powders ($R=1$) calcined at various temperatures for 10 h in air. The crystallinity of the spinel phase increases with increasing temperature as indicated by the intensities of the XRD peaks. For samples calcined below 750°C , an impurity peak related to Mn_2O_3 was detected. The relative intensity of the impurity peak (around $2\theta=33^\circ\text{C}$) increased up to 700°C and then decreased. This impurity phase completely disappears after calcining the sample above 800°C , as the retained Mn_2O_3 has transformed into LiMn_2O_4 , so that the LiMn_2O_4 peaks also become sharper.

Fig. 4 shows the scanning electron micrographs of samples calcined at various temperatures in air for 10 h with the molar ratio of citric acid to the total metal ions fixed at 1. It can be seen that calcined powders are loosely bound agglomerates of

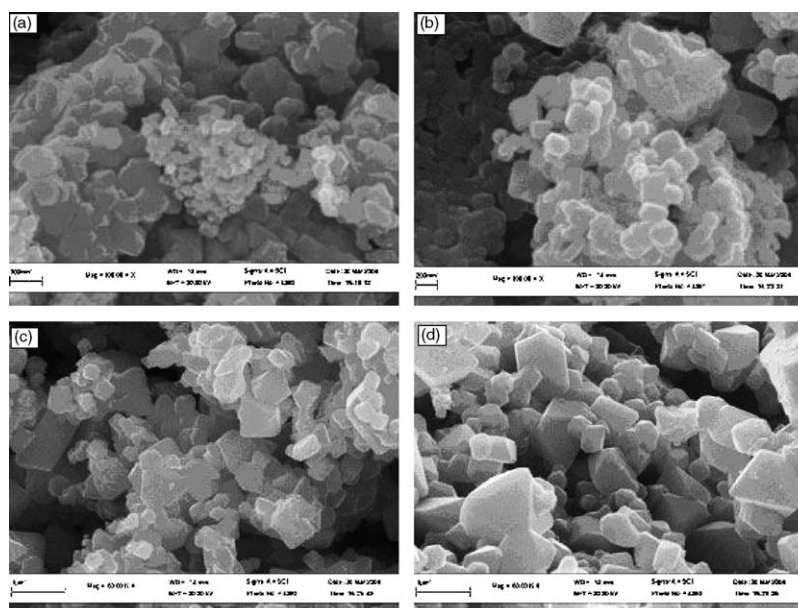


Fig. 4. SEM images of the LiMn_2O_4 calcined at: (a) 750°C , (b) 800°C , (c) 850°C and (d) 900°C .

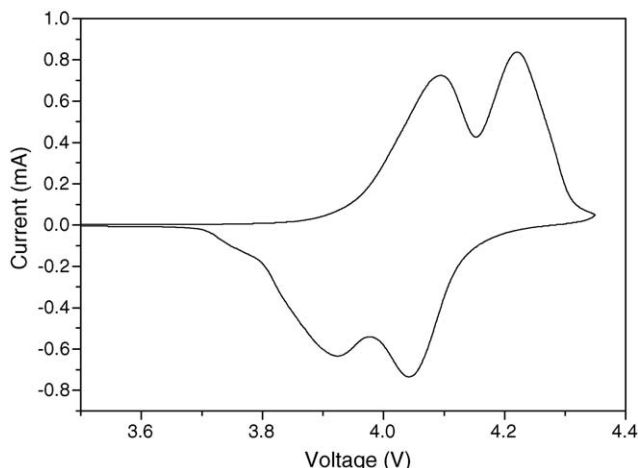


Fig. 5. The cyclic voltammogram of the third cycle for the LiMn_2O_4 calcined at 800°C with $R=1$. Scan rate is 0.1 mV s^{-1} .

uniform particles with a typical crystal shape. The particle size increases as the calcination temperature increases.

Fig. 5 shows the cyclic voltammogram of the third cycle of LiMn_2O_4 with $R=1$ calcined at 800°C at a scan rate of 0.1 mV s^{-1} . Two voltammetric waves are observed indicating phase change of LiMn_2O_4 during the intercalation/deintercalation process. The higher-potential wave corresponds to Li^+ insertion and removal over the x value range of $0 \leq x \leq 0.5$ in $\text{Li}_x\text{Mn}_2\text{O}_4$. The lower potential wave corresponds to Li^+ insertion and removal over the x value range $0.5 \leq x \leq 1$.

Fig. 6 presents the charge/discharge characteristics of LiMn_2O_4 corresponding to Fig. 5. The cell was cycled between 3.0 and 4.35 V. Two potential plateaus located at 3.9 and 4.1 V are observed. These plateau potentials are in good agreement with the potentials of the two voltammetric waves in Fig. 5.

Fig. 7 shows the discharge capacity versus cycle number of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cell at a constant charge/discharge current density of 0.15 mA cm^{-2} and cutoff voltage from 3.0 to 4.35 V for powders calcined at different temperatures. The molar ratio of citric acid to the total metal ions (R) was 1. The single-

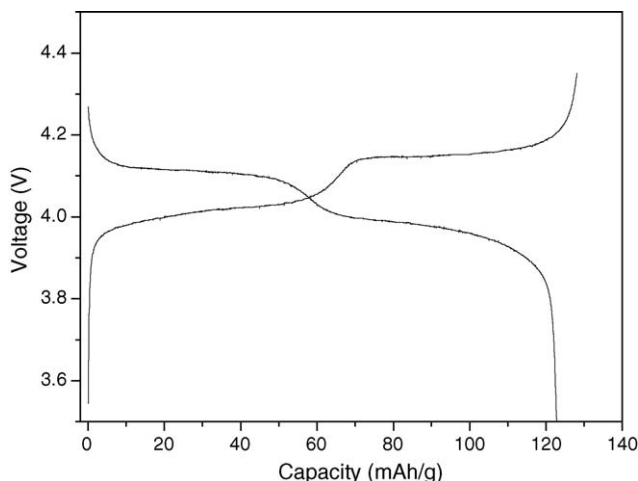


Fig. 6. Charge/discharge curves of the third cycle for the LiMn_2O_4 calcined at 800°C with $R=1$. Scan rate is 0.1 mV s^{-1} .

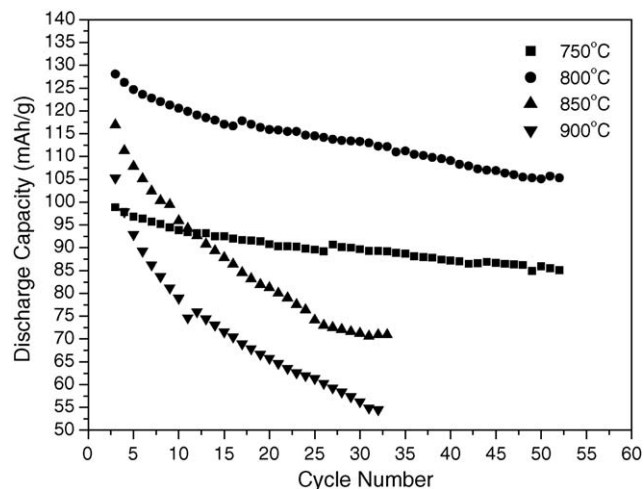


Fig. 7. Specific discharge capacity of LiMn_2O_4 fired at different temperatures, where the molar ratio of citric acid to the total metal ions was 1.

phase LiMn_2O_4 calcined at 800°C initially delivered a discharge capacity of 128 mAh g^{-1} and retained 121 mAh g^{-1} at the 10th cycle and 109 mAh g^{-1} at the 40th cycle. This sample exhibited better capacity retention than that of powders calcined at other temperatures.

Normally, the structure of gel prepared will change with the ratio of the carriers to Li^+ and Mn^+ ions [9], and it can be crosslinked or non-crosslinked. An excess of the polymer carrier is usually used to form a crosslinked structure. If the molar ratio of carrier to total metal ions is too large, the temperature will be raised very high in a short period of time, leading to a decrease of the oxygen partial pressure and the formation of an impurity phase of Mn_2O_3 . When the molar ratio is below 1.0, segregation of the cations occurs, and the combustion heat will be insufficient for the synthesis of LiMn_2O_4 . In this work, citric acid in the reagents works as a carrier and a combustion agent, which forms a crosslinked structure, preventing the aggregation of metal ions. Besides citric acid, cellulose was also added in the reaction systems. Cellulose works as an absorbing agent, which could easily absorb metal ions so that the metal ions

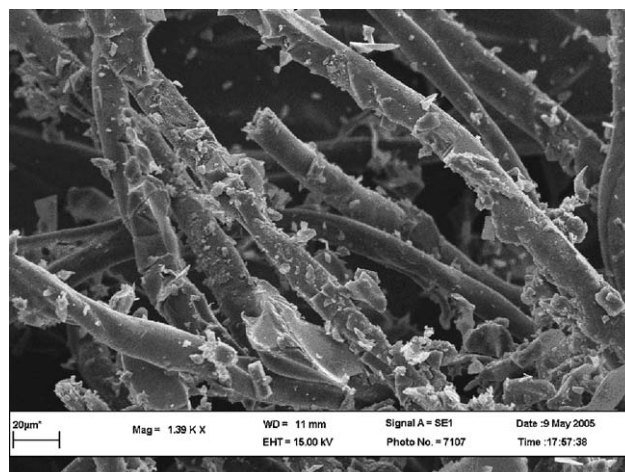


Fig. 8. Scanning electron micrograph of the precursor with $R=1$.

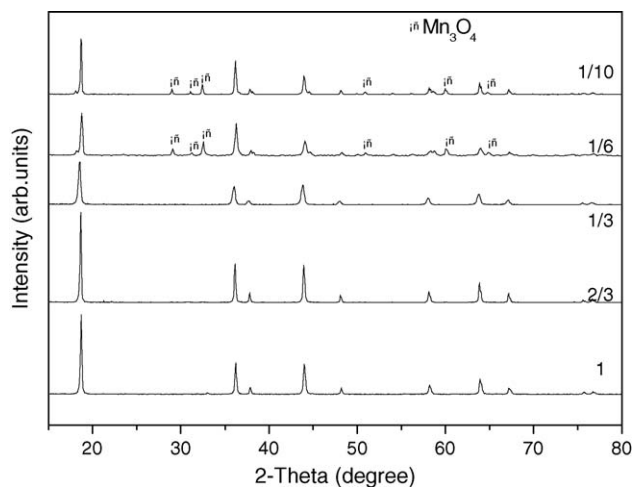


Fig. 9. XRD patterns of LiMn_2O_4 powders calcined at 800°C with different molar ratios.

could be effectively distributed on the surface of cellulose (as shown in Fig. 8). The aggregation of metal ions can be further prevented to some extent. As the decomposition of cellulose and that of citric acid occur in different temperature ranges (as shown in Fig. 1), the coexistence of cellulose and citric acid in the reactive system could achieve a more uniform metal ion distribution during the reaction process than the citric acid only method.

Fig. 9 shows the XRD patterns for the samples calcined at 800°C for 10 h at $R=1$, $2/3$, $1/3$, $1/6$ and $1/10$, respectively. The best crystallinity is observed for the sample with $R=2/3$. The intensity of the LiMn_2O_4 peaks in this sample is higher than that in the sample with $R=1$. When the molar ratio of citric acid to the total metal ions was decreased to $1/6$, a small amount of impurity phase was detected. This phenomenon will be explained in the following paragraph. The average valence of manganese in the reaction products is shown in Table 1.

In order to compare the morphological features of the LiMn_2O_4 powders with different molar ratios of citric acid to the total metal ions, SEM images of powders calcined at 800°C with $R=2/3$ and $1/3$ are shown in Fig. 10. Compared with Fig. 5, the particle size with $R=2/3$ was larger than that with $R=1$. This is caused by the lower amount of citric acid in the precursor, which creates a shorter Li–Mn cation distance,

Table 1
Average valence of manganese in the reaction products

Synthesis temperature ($^\circ\text{C}$)	Molar ratio of citric acid to the total metal ions	Average valence of manganese
800	1	3.46
850	1	3.43
900	1	3.45
800	$2/3$	3.45
800	$1/3$	3.45

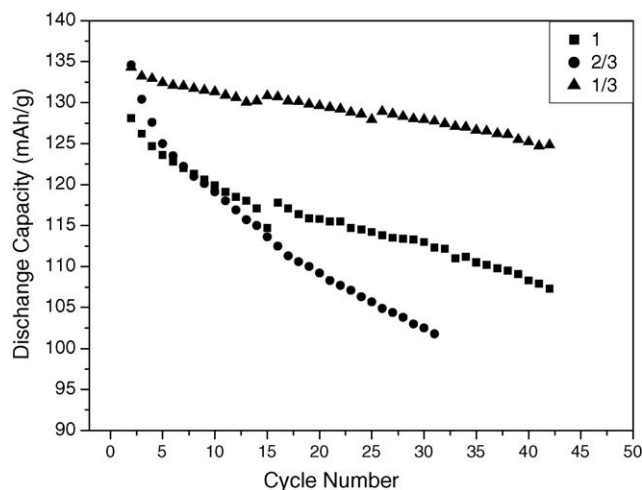


Fig. 11. Specific discharge capacity of LiMn_2O_4 fired at 800°C at various molar ratios of citric acid to the total metal ions.

allowing higher crystallization to be achieved. This results in bigger particles [9]. However, when the molar ratio of citric acid further decreases to $1/3$, the particle size decreases because of the decreased combustion heat generated. If the amount of citric acid is too small, the combustion heat will be insufficient to increase the crystallinity or even to yield the spinel LiMn_2O_4 phase [10].

Fig. 11 shows the discharge capacity versus cycle number of the $\text{Li}/\text{LiMn}_2\text{O}_4$ cell at a constant charge/discharge current density of 0.15 mA cm^{-2} and a cutoff voltage range from 3.0 to 4.35 V for powders calcined at 800°C . The molar ratios of citric acid to the total metal ions were 1, $2/3$ and $1/3$. When the molar ratio was $1/3$, the $\text{Li}/\text{LiMn}_2\text{O}_4$ cell initially delivered

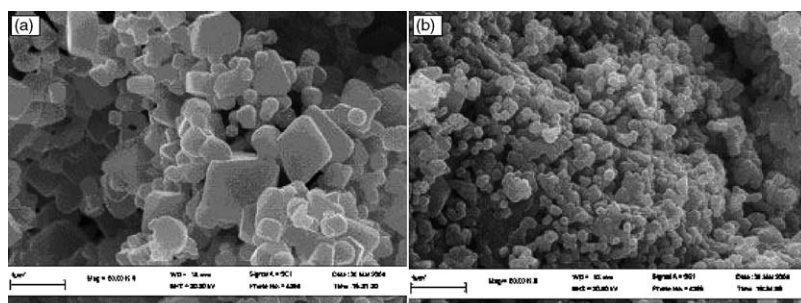


Fig. 10. Scanning electron micrographs of the LiMn_2O_4 calcined at 800°C , with molar ratio (a) $R=2/3$ and (b) $R=1/3$.

134 mAh g⁻¹ and retained 125 mAh g⁻¹ at the 40th cycle. The capacity loss at the 40th cycle was only 6.7%.

4. Conclusion

The cellulose–citric acid method is an effective way to synthesize LiMn₂O₄ compounds with good cyclability. Citric acid in the reagents works as a carrier and a combustion agent, which forms a crosslinked structure, preventing the aggregation of metal ions, while the cellulose in the reagents works as an effective absorbing agent for metal ions, thereby further preventing the aggregation of metal ions. Samples calcined at 800 °C with $R = 1/3$ yield the highest specific capacity of 134 mAh g⁻¹ with only 6.7% loss at the 40th cycle. The LiMn₂O₄ synthesized under optimum conditions could be a promising cathode material for the lithium-ion battery.

References

- [1] A. Yamada, K. Miura, K. Hinokuma, M. Tanaka, J. Electrochem. Soc. 142 (1995) 2149.
- [2] Y. Xia, M. Yoshio, J. Electrochem. Soc. 143 (1996) 825.
- [3] H. Huang, C.A. Vincent, P.G. Bruce, J. Electrochem. Soc. 146 (1999) 481.
- [4] G.G. Amatucci, N. Pereira, T. Zheng, J.M. Tarascon, J. Electrochem. Soc. 148 (2001) A171.
- [5] W. Yang, Q. Liu, W. Qiu, S. Lu, L. Yang, Solid State Ionics 121 (1999) 79.
- [6] B.G. Hwang, R. Santhanam, D.G. Liu, J. Power Sources 101 (2001) 86.
- [7] Y.M. Hon, K.Z. Fang, S.P. Lin, M.H. Hon, J. Solid State Chem. 163 (2002) 231.
- [8] W. Liu, G.C. Farrington, F. Chaput, B. Dunn, J. Electrochem. Soc. 143 (1996) 879.
- [9] Y.K. Sun, I.H. Oh, K.Y. Kim, Ind. Eng. Chem. Res. 36 (1997) 4839.
- [10] H. Taguchi, H. Yoshioka, D. Matsuda, M. Nagao, J. Solid State Chem. 104 (1993) 460.