ELSEVIER

Journal of Power Sources 88 (2000) 274–277

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Short communication

Synthesis and characterization of spinel $LiMn_2O_4$ for lithium secondary battery

Serk-Won Jang [a], Heon-Young Lee [a], Kun-Chul Shin [a], Sung Man Lee [a,*], Jong-Ki Lee [b], Seung-Joo Lee [b], Hong-Koo Baik [b], Dong-Seok Rhee [c]

[a] *Department of Materials Engineering, Kangwon National University, Kangwon, South Korea*
[b] *Department of Metallurgical Engineering, Yonsei University, South Korea*
[c] *Department of Environmental Engineering, Kangwon National University, Kangwon, South Korea*

Received 27 August 1999; accepted 5 December 1999

Abstract

The preparation and characterization of spinel $LiMn_2O_4$ have been studied. Spinel lithium manganese oxides are prepared by a sol–gel method using $LiNO_3$ and $Mn(CH_3COO)_2 \cdot 4H_2O$ as starting materials in which the obtained gel is heated at various temperatures after pretreatment at 350°C or without pretreatment in air. The $LiMn_2O_4$ samples prepared with pretreatment have uniform microsized particles while those obtained without pretreatment have agglomerated particles of irregular shapes. The thermal pretreatment at 350°C improves the electrochemical behaviour in terms of discharge capacity and rate capability. The results can be correlated with an increase in lithium surface reaction sites in these materials, as inferred by this small grain size and large surface area.

Keywords: $LiMn_2O_4$; Pretreatment; Lithium-ion; Particle size; Rechargeable battery; Sol–gel

1. Introduction

Lithium transition metal oxides are candidate cathode materials for lithium-ion rechargeable batteries [1]. Among these oxides, spinel structure Li–Mn–O compounds have attracted a great deal of research because of their economical and environmental advantages.

Preparation of $LiMn_2O_4$ is usually carried out via a solid-state reaction [2]. In this method, a Mn compound and a Li compound are first extensively ground and mixed, and then calcined in air from 750°C to 950°C. The $LiMn_2O_4$, thus obtained, is ground again to the desirable particle size. Solution techniques are often used because the starting components are homogeneously mixed and the synthesis temperature is lowered [3]. The $LiMn_2O_4$ prepared by these methods has agglomerated particles, which are often of irregular shape and have a broad size-distribution. $LiMn_2O_4$ used for rechargeable lithium-ion batteries should be in the form of small, uniformly sized and unagglomerated particles to allow electrochemical discharge over a wide range of rates.

In this paper, we describe a synthetic procedure, using a sol–gel method, which can yield spinel $LiMn_2O_4$ with uniform small particles.

2. Experimental

Manganese acetates and $LiNO_3$ were used for preparing the starting aqueous solutions. The materials were dissolved in ethanol and then the solutions were mixed. The solutions were dried at 90°C under vacuum in a rotating evaporator. After drying, the obtained gel powders were annealed under various conditions of temperature and time. In some cases, the samples were pretreated at 350°C for 48 h in air before heating in the range 650 to 750°C.

The thermal decomposition of the gel powders was studied using a thermal gravimetric analyser with simultaneous recording of weight losses (TGA) and temperature variation (DTA). The phase and crystallinity of the products were examined by means of X-ray diffraction (XRD)

* Corresponding author.
E-mail address: smlee@kangwon.ac.kr (S.M. Lee).

0378-7753/00/$ - see front matter
PII: S0378-7753(00)00374-8

with Cu Kα radiation. The morphologies of the products were observed using a scanning electron microscope(SEM). The specific surface area of the products was determined by the Brunauer–Emmett–Teller (BET) method.

Electrochemical measurements were performed in a Swage lock type cell with EC + DEC/1 M $LiPF_6$ as the electrolyte. Composite cathodes were fabricated by mixing $LiMn_2O_4$, carbon black and polytetrafluoroethylene (PTFE) in the weight ratio 76:12:12. The mixtures were pressed on to an aluminum grid and then the assembly was dried under a vacuum at 120°C for 12 h. All tests were conducted in an argon-filled dry box at room temperature.

3. Results and discussion

The TG–DTA curve for gel powders heated at a rate of 10°C/min in air are given in Fig. 1. There are two endothermic peaks and three exothermic peaks. The endothermic peak, at ~90°C, is related to the evaporation of water adsorbed from the atmosphere. The endothermic peak at 180°C is due to melting of the sintering materials [4]. Very exothermic reactions are observed with concurrent weight loss in the temperature range of 220°C to 350°C. No weight and heat transformations occurred at higher temperatures (until 800°C). This indicates that the decomposition of the gel is complete at 350°C.

The temperature of formation of the $LiMn_2O_4$ phase is strongly related to the heating rate. For example, under static conditions, the phase can be obtained at a temperature which is much lower than that indicated by thermal analysis.

To assess the effect of temperature, $LiMn_2O_4$ was prepared by heating the dried gel powders at 350°C, 600°C and 750°C for 24 h in air. The XRD data (Fig. 2) show that cubic spinel $LiMn_2O_4$ is the only crystalline phase present in the products, and that the XRD peak widths gradually decrease as the annealing temperature increases. The latter indicates the growth of $LiMn_2O_4$ crystallites. Note that the spinel phase forms at 350°C. Analyses of the

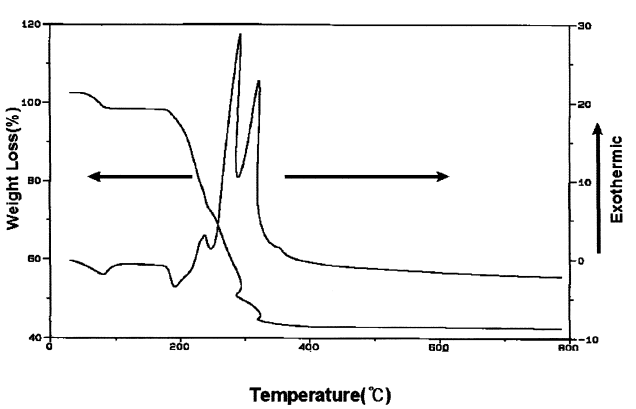

Fig. 1. Thermogravimetric and differential thermal analysis of gel powders at heating rate of 10°C min^{-1}.

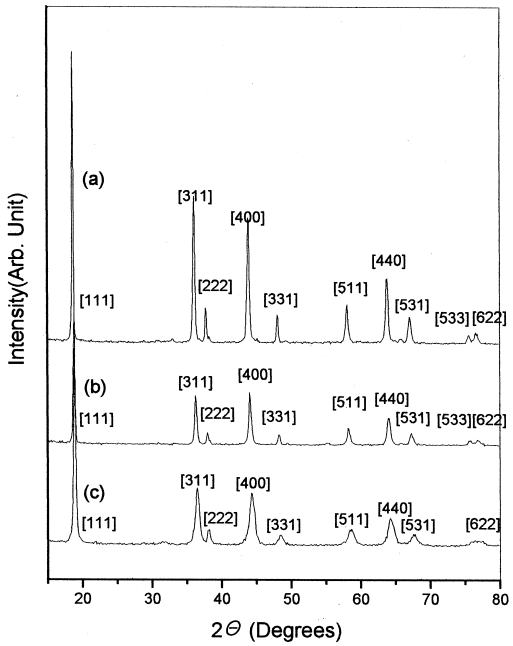

Fig. 2. Power X-ray diffraction patterns of spinel $LiMn_2O_4$ heat treated at various temperatures for 24 h in air: (a) 750°C; (b) 600°C; (c) 350°C.

XRD data by the least-squares method indicate that the lattice parameter of the $LiMn_2O_4$ product increases with the annealing temperature, i.e., the values of the lattice parameter of samples obtained by heating at 350°C, 600°C and 750°C are 8.18, 8.22 and 8.23 Å, respectively. The low lattice parameter of samples prepared at low temperatures can be related to a defect spinel with oxygen deficiency since the LiMn ratio of the samples is 0.5.

It has been also reported that the value of the average oxidation state of manganese in the spinel phase is related to the lattice constant of the cubic unit cell [5]. A lower annealing temperature results in a more oxidized manganese cation because manganese ions are stable as Mn^{4+} at lower temperatures [6].

$LiMn_2O_4$ powders with a wide variety of physicochemical properties such as particle size, crystallinity, specific surface-area and microcrystallite morphologies can be obtained by simply varying the thermal processing, e.g., temperature, time and heating sequence. We have tried to investigate the effects of a thermal pretreatment before the main synthesis on the physicochemical properties and electrochemical behaviour. The thermal pretreatment was performed by heating the dried gel powders at 350°C for 48 h in air. $LiMn_2O_4$ produced by heating in the range 650°C to 750°C after the thermal pretreatment has a larger lattice constant than samples obtained without thermal pretreatment, which indicates an increase in the crystallinity of the spinel powders. The thermal pretreatment also ensures a higher specific surface-area of the final product. This is shown in Fig. 3, which presents the dependence of specific surface-area on the duration of the synthesis at 750°C for the thermally-pretreated sample. For comparison purposes,

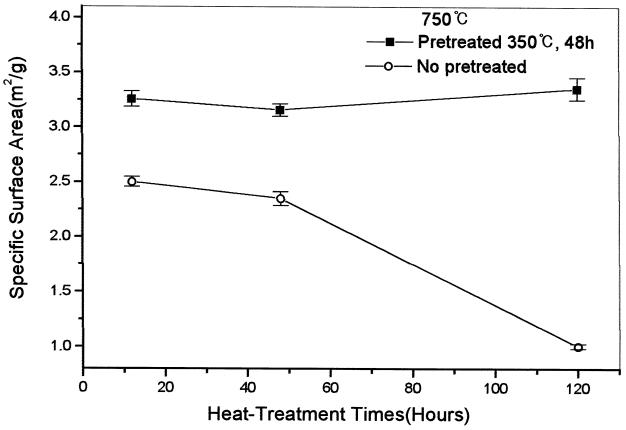

Fig. 3. Dependence of the specific surface-area on the synthesis duration for sample heated at 750°C after thermal pretreatment (350°C, 48 h).

data for $LiMn_2O_4$ synthesized without pretreatment is also given. It should be noted that for the thermally-pretreated sample, there is little change in specific surface-area during heating at 750°C up to 120 h. SEM studies show that the thermally-pretreated sample possesses small, uniformly sized and unagglomerated particles during the synthesis, while $LiMn_2O_4$ prepared without pretreatment consists of large, strongly agglomerated particles. These morphological features are more evident in Fig. 4, which gives electron micrographs for the samples obtained after heating at 750°C for 120 h.

The resulting $LiMn_2O_4$ powders prepared at various temperatures in the range 350°C to 750°C were examined for their lithium intercalation properties. The assembled cells were charged and discharged between cut-off voltages of 3.5 and 4.5 V at a constant current rate. The discharge capacity increases with the synthesis temperature (data not shown here). This can be related to the low crystallinity and defects in the structure of the samples synthesized at low temperatures. Thermal pretreatment at lower temperature (350°C, 48 h), in combination with a following synthesis at 650°C to 750°C, improved the electrochemical behaviour of the samples such as the discharge capacity and rate capability. The effect of varying the discharge rate on the specific discharge capacity is presented in Fig. 5 for $LiMn_2O_4$ obtained at 750°C. It is evident that thermal pretreatment leads to an increase in the discharge capacity and an improvement in the rate capability. This can be explained by a difference in the size and uniformity of the particles. Note also that for the pretreated samples, longer heat-treated $LiMn_2O_4$ exhibits better rate capability, although the particle size and specific surface-area of the powders are similar. This seems to be associated with an increase in the lattice constant, i.e., crystallinity. From the above results, it can be considered that thermal pretreatment plays an important role in the preparation of $LiMn_2O_4$ powders using a solution process. Therefore, it is appropriate to find a more suitable combination of synthesis duration and temperature for a better

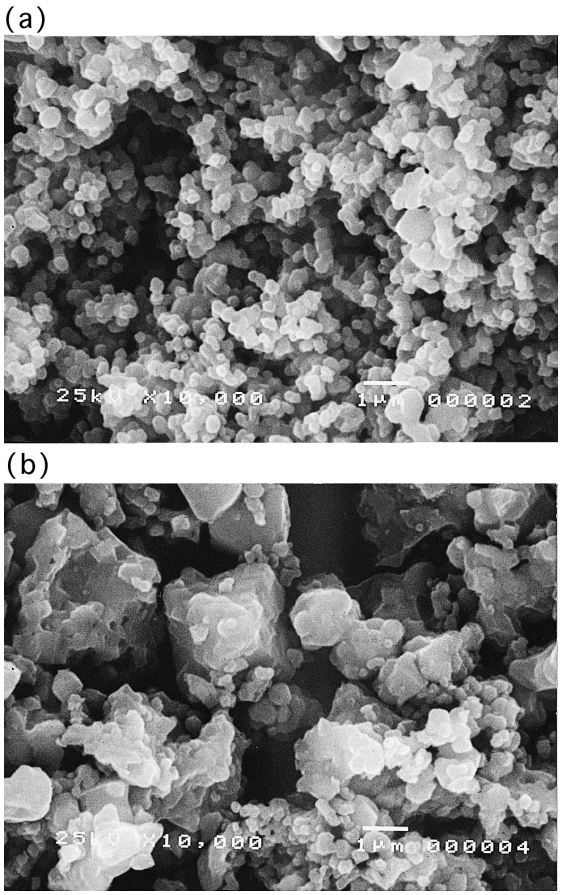

Fig. 4. SEM Image of $LiMn_2O_4$: (a) heat-treated at 750°C for 120 h after pre-treatment; (b) heat-treatment at 750°C for 120 h without pre-treatment.

electrochemical performance. At present, however, the mechanism of the pretreatment, however, is not clear.

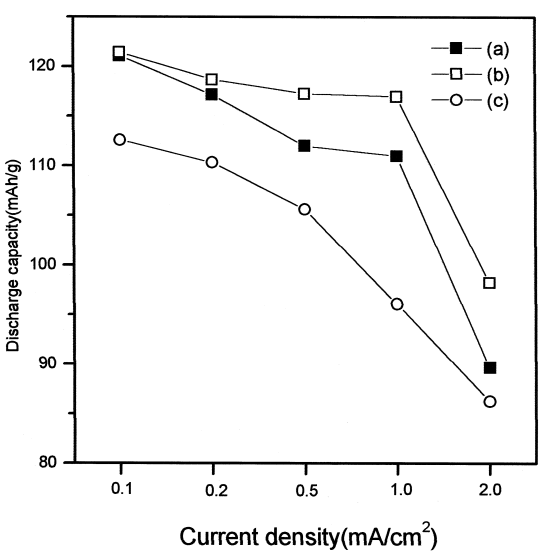

Fig. 5. Graph of discharge capacity for several current densities for a $Li/LiMn_2O_4$ cell using $LiMn_2O_4$ prepared by: (a) heating at 750°C for 48 h after pretreatment: (b) heating at 750°C for 120 h after pretreatment: (c) heating at 750°C for 120 h without pretreatment.

4. Conclusions

A spinel $LiMn_2O_4$ compound has been synthesized by a solution method, in which dried gel powders are heat-treated for various times at temperatures between 350°C and 750°C. In the synthesis process, thermal pretreatment of the dried gel powders at 350°C for 48 h leads to $LiMn_2O_4$ with small, uniformly sized, and unagglomerated particles. This improves the electrochemical behaviour of the samples.

Acknowledgements

This work was financially supported by the Korea Science and Engineering Foundations under contract No. 966-0300-006-2.

References

[1] T. Ohzuku, in: G. Pistoia (Ed.), Lithium batteries : New Materials, Development and perspectives, Elsevier, New York, 1994, p. 239.
[2] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, J. Electrochem. Soc 138 (1991) 2859.
[3] K. Amine, H. Tukamoto, H. Yasuda, Y. Fujita, J. Electrochem. Soc 140 (1996) 1607.
[4] P. Barboux, J.M. Tarascon, F.K. Shokoohi, J. Solid State Chem 94 (1991) 185.
[5] J.M. Tarascon, W.R. Mckinnon, F. Coowar, T.N. Bowmer, G. Amatucci, D. Guyomard, J. Electrochem. Soc 141 (1994) 1421.
[6] C. Masquelier, M. Tabuchi, K. Ado, R. Kanno, Y. Kobayashi, Y. Maki, O. Nakamura, J.B. Goodenough, J. Solid State Chem 123 (1996) 225.