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Journal of Power Sources 97–98 (2001) 443–446

JOURNAL OF
**POWER
SOURCES**

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Characterization of nanoparticles of LiMn_2O_4 synthesized by citric acid sol–gel method

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Received 28 June 2000; received in revised form 3 November 2000; accepted 29 December 2000

Abstract

Nanoparticles of lithium manganese oxide (LiMn_2O_4) spinel oxides have been synthesized from aqueous solutions of metal acetate containing citric acid as a chelating agent by a sol–gel method. The influence of calcination temperature on the physicochemical properties of LiMn_2O_4 powders in air atmosphere has been analyzed by means of X-ray diffraction (XRD) and electron microscopic techniques. The thermal behavior of the material has been examined by thermogravimetry (TG) and differential thermal analysis (DTA). Two sharp and well-defined peaks obtained from cyclic voltammetry of Li/1 M $\text{LiPF}_6\text{-EC/DEC}$ electrolyte/ LiMn_2O_4 cell reveal that the LiMn_2O_4 particles are highly crystalline and insertion–extraction mechanism occur at two stages in the 4 V region. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: LiMn_2O_4 ; Sol–gel synthesis; Citric acid

1. Introduction

Lithium manganese oxide (LiMn_2O_4) has been studied extensively as a potential cathode material for lithium rechargeable batteries due to its low cost, limited environmental impact and excellent voltage profile characteristics [1–5]. However, in comparison with layered oxides such as LiCoO_2 and LiNiO_2 , LiMn_2O_4 has problems related to capacity fading and limited cycleability in the 4 V region. The reason for capacity fading has not yet been fully understood but some possible mechanisms have been proposed as (i) dissolution of manganese spinel into the electrolyte, (ii) decomposition of the electrolyte on the surface of the cathode at the fully charged state and (iii) breakdown of the spinel framework due to repeated lattice contraction–expansion [6–10]. However, the dissolution of spinel has only a minor influence on cathode cycleability [11].

It is known that particle size and surface morphology have an influence on the charge–discharge rate capability, safety cell performance and electrode formulation of the cathode material [9,10,12,13]. In particular, a decrease in mean particle size results in an increase in the cycleability and rate capability of the cathode material because smaller particles are more flexible than larger particles [14].

Furthermore, during cycling the changes in the lattice parameters do not affect the cycleability of the smaller particles to the degree that larger particles are affected [14]. The cathode cycleability is also affected by the dissolution of spinel. Synthesis of LiMn_2O_4 by conventional solid state method is not relevant to control particle size because it involves high temperature, long and repeated heat treatments, and extended grinding. This method also has several disadvantages, such as inhomogeneity, irregular morphology, large particle size and broad particle size distribution and poor control of stoichiometry. Now, solution method has been proposed for the preparation of high performance cathode materials for lithium batteries [15–18]. This method has advantages such as good control of stoichiometry, lower calcination temperature, relatively shorter processing time and production of submicron sized particles with narrow particle size distribution.

In this work, LiMn_2O_4 powders were synthesized by a sol–gel method using citric acid as a chelating agent. The main aim of this work is to synthesize LiMn_2O_4 powders with smaller particle size and their characterization.

2. Experimental

LiMn_2O_4 powder was synthesized by sol–gel method using citric acid as a chelating agent. The citrate precursor was obtained by this method as described as follows. At first,

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manganese acetate was dissolved in deionized water to give a saturated solution. To this solution, lithium acetate was added slowly with mild stirring. A saturated aqueous solution of citric acid was then added at a molar ratio of Li:Mn: citric acid = 1:2:3. The pH of the mixed solution was maintained at 7.0 by adding ammonium hydroxide solution. Then the solution was heated to 80°C for 4 h with vigorous stirring to remove excess ammonia and water. The metal citrate precipitate formed was dried in air oven for 10 h at 100°C. After drying, the precursors were decomposed at 300°C for 6 h in air to eliminate organic contents. The decomposed powders were slightly ground and then calcined at different temperatures viz., 300, 400, 500, 600, 700 and 800°C in air. During heating and cooling, the temperature variation was fixed at 1°C/min.

The chemical composition of the spinel sample was analyzed by using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements. The thermal decomposition behavior of the citrate precursor was examined by thermogravimetry (TG) and differential thermal analysis (DTA) by means of a thermal analyzer (Ulvac Sinku-Riko TG-7000). Powder X-ray diffraction (XRD, Rigaki) using Cu K α radiation was used to identify the crystalline phase of the materials calcined at various temperatures. The particle morphology of the materials was observed by scanning electron microscopy (SEM) using a Hitachi S-2400 and transmission electron microscopy (TEM) using a JEOL JSM 1200 Ex II.

The cyclic voltammetric studies were carried out in an electrochemical cell consisted of LiMn₂O₄ powder synthesized by sol-gel method and a commercial powder received from sedema, Belgium as cathodes, lithium metal as an anode and an electrolyte of 1 M LiPF₆ in a 1:1 (v/v) mixture of ethylene carbonate (EC)/dimethyl carbonate (DEC). The cathode was a mixture of 80 wt.% active material, 10 wt.% carbon black and 10 wt.% polyvinylidene fluoride binder. The composition of the composite cathode prepared by the synthesized and commercial powder is the same. The cells were assembled in an argon-filled dry box where both moisture and oxygen contents were <1 ppm. Cyclic voltammetry scans were recorded from 3.6 to 4.5 V at a scan rate of 0.02 mV/s at room temperature. Lithium metal served as both counter and reference electrodes.

3. Results and discussion

The thermal behavior of the citrate precursor was measured using TG and DTA. Three main weight loss regions are observed in the temperature range 150–370°C. The weight loss in the temperature range of 150–220°C and an endothermic peak are due to the removal of water. The weight loss in the temperature range of 220–320°C is associated with the decomposition of citric acid, citrates and manganese acetate ions. The weight loss in the temperature range of 320–370°C is due to the decomposition of

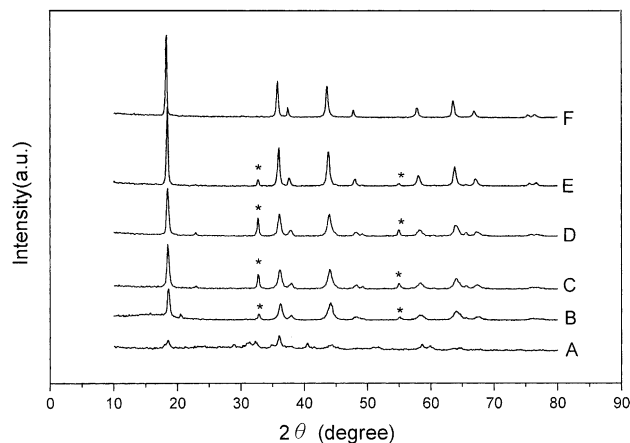


Fig. 1. Powder XRD patterns of LiMn₂O₄ prepared in air at (°C): (A) 300; (B) 400; (C) 500; (D) 600; (E) 700 and (F) 800. The peaks corresponding to Mn₂O₃ phase are marked with asterisk (*).

lithium acetate ions and acetic acid. Two exothermic peaks are appeared corresponding to these two weight loss regions. A slight weight decrease in the temperature above 370°C is attributed to combustion of remaining organic constituents. It seems that the citric acid functions as a fuel in the decomposition of acetate ions and the heat evolved from the decomposition of acetate ions accelerates the decomposition of the remaining organic constituents.

Fig. 1 shows XRD patterns for citrate precursors calcined at various temperatures in air. The crystallinity of spinel phase calcined at 300°C is poor. However, the crystallinity is increased with increasing temperature as indicated by the sharpness of the intensities of the XRD peaks. The impurity peaks observed in the XRD patterns are due to the formation of Mn₂O₃ during firing. Since carbon-containing raw materials, lithium acetate and manganese acetate, have been used to synthesize LiMn₂O₄, it seems that the large amount of carbon content in the precursor tends to reduce the manganese ions during firing and favors the formation of Mn₂O₃ impurity [19].

The variation of particle size and morphology on the calcination temperatures has been examined by SEM. SEM micrographs reveal that the particles exhibit uniform crystal shape and good crystallinity with an average size of <100 nm. The samples calcined at low temperatures consisted of smaller particles. As the calcination temperature increases, the particle size also increases. In particular, at 800°C the particles exhibit good crystallinity and uniformity. These results are consistent with the results obtained from XRD measurements. Fig. 2 shows the TEM image obtained for the sample calcined at 800°C. This image exhibit a substantial particle agglomeration due to high degree of crystallization at high temperature.

The electrochemical behavior of LiMn₂O₄ sample calcined at 800°C was characterized by cyclic voltammetry as shown in Fig. 3a. Cyclic voltammogram was recorded at a scan rate of 0.02 mV/s in 1 M LiPF₆ in a 1:1 (v/v) mixture of



Fig. 2. Transmission electron micrographs for LiMn_2O_4 particles synthesized and calcined at 800°C .

EC/DEC between 3.6 and 4.5 V. The anodic and cathodic peaks observed in the cyclic voltammogram of the LiMn_2O_4 sample reflect reversible oxidation and reduction reactions corresponding to lithium extraction and insertion. Two separated pairs of electrochemical peaks are seen for both oxidation and reduction, indicating that the insertion and extraction of lithium ions occur in two stages [20]. The first peak at about 4.05 V is attributed to the removal of lithium ions from half of the tetrahedral sites in which Li–Li interactions occur. The second peak observed at about 4.18 V is due to the removal of lithium ions from the other tetrahedral sites in which lithium ions do not have Li–Li interactions. The area of two oxidation and reduction peaks are essentially equal which indicates that in each stage lithium ions occupy half of the total available

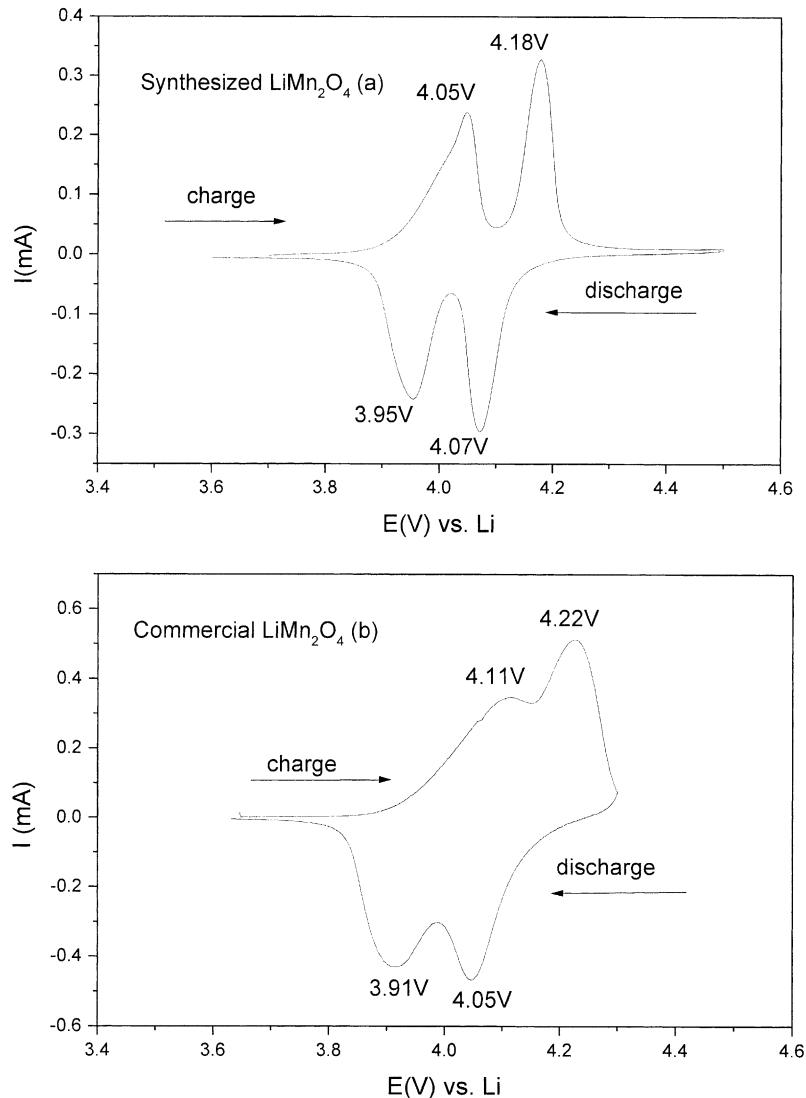


Fig. 3. Cyclic voltammogram of (a) LiMn_2O_4 synthesized and calcined at 800°C and (b) LiMn_2O_4 commercial; scan rate: 0.02 mV/s.

crystallographic sites. Moreover, the peaks are sharp and show well-defined splitting. These are the characteristics of the materials with high degree of crystallinity [21]. This observation is consistent with the results obtained from XRD and SEM measurements.

A typical cyclic voltammogram obtained for commercial LiMn_2O_4 powder is presented in Fig. 3b to compare the electrochemical behavior of synthesized LiMn_2O_4 powder. In this commercial powder, also two separated electrochemical peaks are seen for oxidation and reduction. However, the peak potentials are varied slightly, the peaks are not sharp and splitting of the peaks is not well-defined when compared to synthesized powder. This results that the synthesized powders are more crystalline than commercial powder. In the commercial powder, removal of lithium ions with no Li–Li interactions occurs before lithium ions with Li–Li interactions are completely removed. Therefore, clearly separated peaks are not observed for commercial powder (Fig. 3b). The peak potentials difference between synthesized and commercial powder is due to difference in energy of lithium ions in the tetrahedral sites, which depends on the energy of bond between lithium and its neighbors. Hence, it is believed that the removal of lithium ions from the tetrahedral sites requires more energy for commercial powder than synthesized powder.

4. Conclusions

The sol–gel method using citric acid as a chelating agent was found to be an effective method for synthesizing nanocrystals of LiMn_2O_4 -based cathode materials for lithium batteries. In the present work, the spinel LiMn_2O_4 powders with nanosized particles were synthesized at 300–800°C for 6 h in air by the sol–gel method using an aqueous solution of metal acetate containing citric acid as a chelating agent. The crystallinity of the LiMn_2O_4 powders synthesized increased with increasing calcination temperature. Two sharp and well-defined peaks observed in cyclic voltammograms also indicated that the LiMn_2O_4 powder synthesized were highly crystalline and insertion–extraction reaction

occur at two stages. The studies on charge–discharge cycle life of this material are underway.

Acknowledgements

The financial support from National Science Council (NSC 89-2214-E-011-012 and NSC 89-TPC-7-011-008) and National Taiwan University of Science and Technology is gratefully acknowledged.

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