

Nano Crystalline Manganese Spinel LiMn₂O₄ Prepared by Ultrasonic Spray Pyrolysis

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Introduction

Manganese spinel LiMn₂O₄ and its derivatives are the most attractively studied cathode materials for lithium secondary batteries because of their three dimensional Li⁺ diffusion, low cost, abundance, and nontoxicity [1,2]. Recently, nanocrystalline metal oxides have been studied as promising alternative cathode materials to overcome the severe capacity loss and improve structural stability in the 3 V range, since this type of materials are much more stable compared with microcrystalline one that suffer from the structural transition during repeated electrochemical cycling; Synthesis of nanocrystalline cathode materials have been reported in the literature by use of various solution methods such as sol-gel, coprecipitation, and hydrothermal. In this work, nano-sized spinel LiMn₂O₄ powders have been synthesized by ultrasonic spray pyrolysis and studied nanocrystalline cathode features in the 3 V range.

Experimental

Nano-sized LiMn₂O₄ was prepared by the ultrasonic spray pyrolysis. A stoichiometric amount of lithium nitrate and manganese nitrate were dissolved in distilled water. The dissolved solution was added into a continuously agitated aqueous citric acid solution. The starting solution was atomized using an ultrasonic nebulizer with a resonant frequency of 1.7 MHz. The aerosol stream was introduced into the vertical quartz reactor heated at 500 °C. The flow rate of air used as a carrier gas was 10 L min⁻¹. The prepared powders were further calcined at 500 °C for 5 h in air.

Results and discussion

Figure 1 shows X-ray diffraction patterns of LiMn₂O₄ powders prepared different calcinations temperature. All samples can be indexed based on a cubic spinel structure with a space group of *Fd3m*. No impurity peaks are observed from the XRD pattern. Figure 2 shows SEM and TEM images of the nanocrystalline LiMn₂O₄ powders. The powders have spherical particle shape with a mean diameter of 2 μm. In Figure 2b, the particle seen in a bright field mode clearly shows that the spherical particle is not hollow judging from the solid contrast observed throughout the particle. Figure 3 shows the charge/discharge curves of

the Li/LiMn₂O₄ cell. The LiMn₂O₄ electrode calcined 500 °C exhibited stable cycling behaviors on the 3 V region. The initial discharge capacity of the LiMn₂O₄ electrode was 125 mAh/g, and the capacity retention after 50 cycles was 97 %.

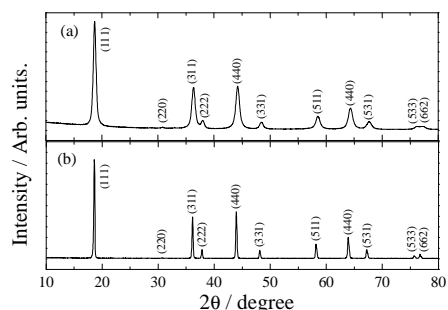


Figure 1. Figure 1. X-ray diffraction patterns of the LiMn₂O₄ powder calcined at (a) 500 and (b) 800 °C.

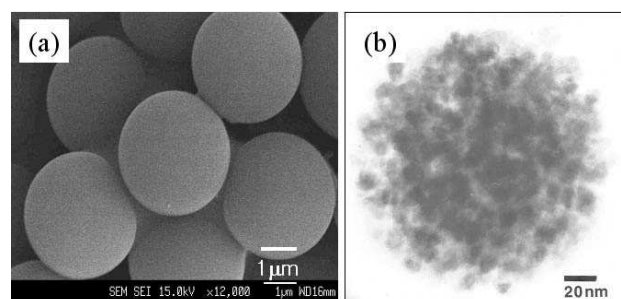


Figure 2. (a) SEM and (b)TEM images of the LiMn₂O₄ powder calcined at 500 °C.

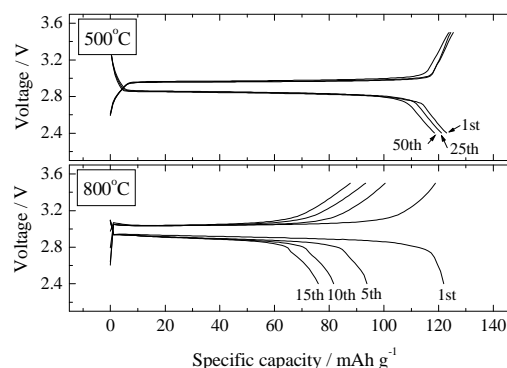


Figure 3. Charge/discharge curves of the Li/LiMn₂O₄ cell between 2.4 and 3.5 V at a constant current density of 20 mA g⁻¹.

Acknowledgements

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References

- [1] M. M. Thackeray, *Prog. Solid State Chem.* **25**, 1 (1997).
- [2] R.J. Gummow, A. Kock, M.M Thackeray, *Solid State Ionics*, **69**, 59 (1994)