



Synthesis of spinel LiMn_2O_4 with manganese carbonate prepared by micro-emulsion method

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ABSTRACT

Micro-spherical particle of MnCO_3 has been successfully synthesized in CTAB- C_8H_{18} - $\text{C}_4\text{H}_9\text{OH}$ - H_2O micro-emulsion system. Mn_2O_3 decomposed from the MnCO_3 is mixed with Li_2CO_3 and sintered at 800°C for 12 h, and the pure spinel LiMn_2O_4 in sub-micrometer size is obtained. The LiMn_2O_4 has initial discharge specific capacity of 124mAh g^{-1} at discharge current of 120mA g^{-1} between 3 and 4.2 V, and retains 118mAh g^{-1} after 110 cycles. High-rate capability test shows that even at a current density of 16 C, capacity about 103mAh g^{-1} is delivered, whose power is 57 times of that at 0.2 C. The capacity loss rate at 55°C is 0.27% per cycle.

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1. Introduction

Lithium manganese oxide LiMn_2O_4 is a promising cathode material for lithium secondary batteries from the viewpoints of the low cost and environmental suitability of the material. Another advantage of using the LiMn_2O_4 is based on its high cell voltage so that it has been considered as a cathode material for high-power lithium battery applications. The material suffers, however, from insufficient cycling stability and structural instability for high-temperature applications [1–4].

Generally, the electrochemical performance of electrode materials is closely associated with the phase crystallinity, purity, particle size and distribution. From various synthetic methods reported in the previous literatures, the results clearly indicated that the physicochemical properties of the resulting product including structure, purity, morphology, and electrochemical performance are greatly influenced by the precursor or starting materials [5–7].

It is well known amongst battery material scientists that particle size affects the electrochemical performance of cathode materials in Li-ion cells [8–10]. Small cathode active particles provide short diffusion pathways, resulting in an improvement in lithium-ion intercalation kinetics [11], which should allow for higher discharge rates and minimize structural distortion at the surface of the cathode grains, which are related to capacity fade [12–14].

Bao et al. reported that LiMn_2O_4 prepared from $\gamma\text{-MnOOH}$ has a loose, porous, cluster-like structure that consists of regular nanometer particles, and provides enhanced cycleability [7]. In reference [15], homogeneous nanocrystalline LiMn_2O_4 was prepared from $\alpha\text{-MnO}_2$ nanorods synthesized by a hydrothermal route that exhibited good cycleability and high-rate capability, with 120mAh g^{-1} at 20mA g^{-1} , and about 90mAh g^{-1} at 240mA g^{-1} . Lu and Fey prepared nanometer size of LiMn_2O_4 by solution combustion method, which shows better electrochemistry performance than a commercial sample [16].

Micro-emulsions are thermodynamically stable system consisting of two or more immiscible liquids, such as oil and water, with the addition of amphiphilic surfactant. In the water in oil type (reverse) of micro-emulsion, aqueous droplets with certain dimension, normal in nanometer size, are enclosed in continued oil phase. In the micro-emulsions, not only the small size and shape can be precisely controlled, but the better size distribution can also be obtained. This character has been used successfully to produce AgBr, cobalt boride, molybdenum sulfide and silica/cadmium sulfide nanometer composites [17–20]. Kim and co-workers synthesized $\text{LiMn}_{2-x}\text{Ni}_x\text{O}_4$ and $\text{LiMn}_{2-x}\text{Fe}_x\text{O}_4$ in the Span 80-kerosene-paraffin oil micro-emulsion system [21,22]. In their experiments, the emulsion of mixed Li^+ , Mn^{2+} and Ni^{2+} salt solutions was converted into ultrafine droplets with homogeneous composition. Then the water and petroleum were evaporated by placing the mixture in petroleum heated at 170°C , and the gotten powder was calcined at high temperature to obtain aimed products. Though the average particle size of pure LiMn_2O_4 was about 200 nm, the discharge capacity of cathode material dropped

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sharply from 123.7 to 93.7 mAh g⁻¹ after 30 cycles between 3 and 4.5 V. Seen from their SEM photo, the particle is not homogeneous and has obvious aggregation. Hwang et al. also synthesized sub-micrometer LiMn₂O₄ particle with highly uniform in size in the Tween 85-kerosene emulsion system [23], but presented only the initial discharge capacity of 115 mAh g⁻¹ and not other electrochemical data.

The homogenous aqueous droplets of water in oil type micro-emulsion could also be used as reaction sites [24–26]. When two micro-emulsions with same composition were mixed under constant stirring, due to the frequent collisions of the aqueous cores of water-in-oil micro-emulsions [27,28], the reacting species in the two micro-emulsions come into contact and react. The growth of particles of chemical reaction product is limited within the nanosize aqueous droplets of the micro-emulsion. Then small and homogeneous product particles will be gotten.

In this work we reported on the synthesis of spherical MnCO₃ particles by a micro-emulsion route. For accurate measure, MnCO₃ was decomposed to Mn₂O₃ and mixed with Li₂CO₃, the mixture was then sintered at high temperature to obtain spinel LiMn₂O₄. The electrochemical performances of the prepared LiMn₂O₄ are investigated.

2. Experimental

2.1. Synthesis

Water in oil type of CTAB–C₈H₁₈–C₄H₉OH–H₂O micro-emulsion was used as reaction system because of its high water/oil ratio and abundant phase diagram data. Cetyltrimethyl ammonium bromide (C₁₆H₃₃N(CH₃)₃Br, CTAB) is a surfactant, *n*-octane (C₈H₁₈) is an oil phase, *n*-butanol (C₄H₉OH) is a cosurfactant, 0.3 mol L⁻¹ Mn(NO₃)₂ or 0.6 mol L⁻¹ NH₄HCO₃ was an aqueous phase, respectively. The mass ratio was $m_{\text{CTAB}} : m_{\text{C}_8\text{H}_{18}} : m_{\text{C}_4\text{H}_9\text{OH}} : m_{\text{aq}} = 12 : 44 : 10 : 34$.

Two micro-emulsion systems, containing Mn(NO₃)₂ or NH₄HCO₃ aqueous solution respectively, became homogeneous and transparent by mixing with motor. Then the micro-emulsion containing Mn(NO₃)₂ was dropped into the micro-emulsion containing NH₄HCO₃ with continuous mixing, brown deposit formed at once. After the deposition reaction finished, the precipitate was centrifuged at 4500 rpm rate, and was then washed with a 1:1 mixture of methanol and chloroform (CH₃OH–CHCl₃), followed by pure methanol (CH₃OH) and deion water (H₂O) in turn, to remove any oil, surfactant and impurity salt from the particles. The brown precipitate was dried at 100 °C for several hours in a vacuum oven. Sintering of particles is not expected at this temperature. Then a light brown precursor was gotten.

For preparing LiMn₂O₄ with accurate stoichiometric proportion, the light brown precursor (MnCO₃) was decomposed at 650 °C for 2 h, and black powder (Mn₂O₃) was produced. The mixture of Mn₂O₃ and Li₂CO₃ (Li/Mn = 1.02:2) was mixed with a mortar and pestle, then ground thoroughly and calcined at 750, 800 or 850 °C for 12 h in air with a heating rate of 10 °C min⁻¹. After cooling in stove, the final black powder (LiMn₂O₄) was gotten.

2.2. Characterization

In order to identify the crystal structure and the purity of the samples, X-ray diffraction (XRD) analysis was performed by using a Philips X'Pert MPD (Philips) instrument with Cu K_α radiation. Scanning electronic microscopy (SEM) was performed by using a JSM-5600LV (JEOL) instrument to detect the surface morphology and analyze the size of the particles. To determine the chemical composition, Li and Mn concentration of LiMn₂O₄ were measured by inductively coupled plasma (ICP, Optima 4300DV, PE

Ltd.). BET surface area measurements were done by the nitrogen adsorption–desorption method (Monosorb, Quanta Chrome Ltd.).

2.3. Electrochemical characterization

The charge–discharge properties of LiMn₂O₄ were investigated in CR2025 coin-type cells. A composite positive electrode was built by mixing the LiMn₂O₄ powders, a black carbon, and a PVDF binder in a weight ratio of 85:10:5. These were then coated onto an Al foil current collector and dried at 120 °C for 10 h in a vacuum oven. Circular discs with a diameter of 10 mm were punched out as the positive electrode. A typical disk electrode contains 8 mg of active material with a thickness of 80 μm. A disk of lithium foil was used as the negative electrode. As a separator we used a piece of Celgard 2400 membrane. 1 M LiPF₆/EC + DMC (50:50 vol%, Guotai, China) was applied as the electrolyte. The test cells were assembled in a glove box with an excellent environment control, the concentration of both H₂O and O₂ were below 1 ppm. The charge–discharge performance of the cells was conducted on a battery test system (Land CT 2001A, Land Co. China).

3. Results and discussion

3.1. MnCO₃ and Mn₂O₃

Fig. 1a shows the XRD pattern of the light brown precursor prepared by micro-emulsion method, which fit well with the standard pattern of MnCO₃ (JCPDS No. 07-0268). Fig. 2a and c show the SEM of this precursor, it could be found that the MnCO₃ are homogeneous spherical morphology with uniform particle size distribution of 2–3 μm, which were accumulated helically by sheets. This kind of morphology of helical spheres obviously came from the limited growing space in the micro-emulsion droplets and strong mixing.

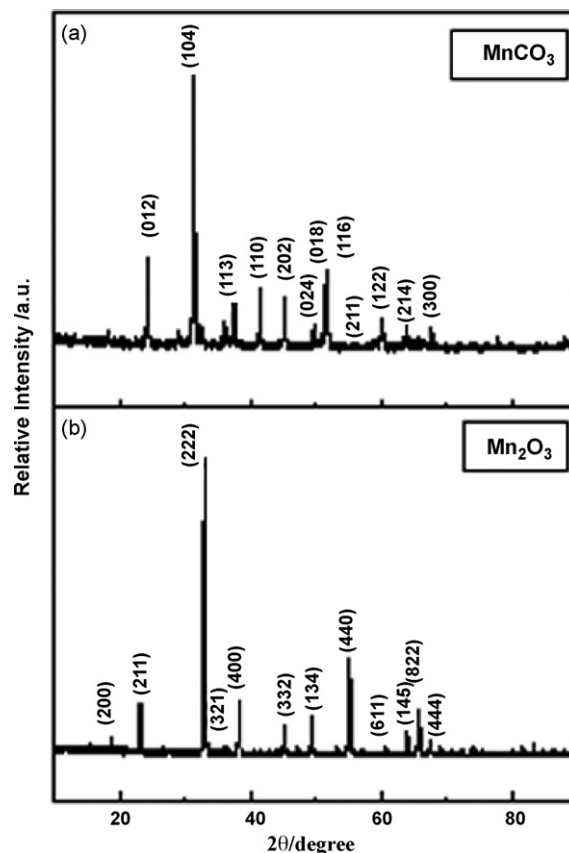


Fig. 1. XRD patterns of (a) the yellow precursor and (b) the blank powder.

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