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Electrochemical performance of spinel $LiMn_2O_4$ cathode materials made by flame-assisted spray technology

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ABSTRACT

Spinel lithium manganese oxide $LiMn_2O_4$ powders were synthesized by a flame-assisted spray technology (FAST) with a precursor solution consisting of stoichiometric amounts of $LiNO_3$ and $Mn(NO_3)_2{\cdot}4H_2O$ dissolved in methanol. The as-synthesized $LiMn_2O_4$ particles were non-agglomerated, and nanocrystalline. A small amount of $Mn_3O_4$was detected in the as-synthesized powder due to the decomposition of spinel $LiMn_2O_4$ at the high flame temperature. The impurity phase was removed with a post-annealing heat-treatment wherein the grain size of the annealed powder was 33 nm. The charge/discharge curves of both powders matched the characteristic plateaus of spinel $LiMn_2O_4$ at 3 V and 4 V *vs.* Li. However, the annealed powder showed a higher initial discharge capacity of 115 mAh g^{-1} at 4 V. The test cell with annealed powder showed good rate capability between a voltage of 3.0 and 4.3 V and a first cycle coulombic efficiency of 96%. The low coulombic efficiency from capacity fading may be due to oxygen defects in the annealed powder. The results suggest that FAST holds potential for rapid production of uniform cathode materials with low-cost nitrate precursors and minimal energy input.

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1. Introduction

Spinel lithium manganese oxide $LiMn_2O_4$ and its derivatives have gained attention as an alternative to lithium cobalt oxide ($LiCoO_2$), which is currently being used commercially as a cathode material for lithium-ion secondary batteries. Spinel $LiMn_2O_4$ has many desirable advantages, including high rate performance due to its 3D framework, high energy density, low cost, low toxicity, and simplicity of preparation [1]. The conventional approach to synthesis of $LiMn_2O_4$ spinel is the solid-state reaction of a mixture of lithium and manganese precursors at high temperature [2]. Sometimes mechanical grinding (*e.g.,* ball milling) is needed to reduce particle size [3]. Other approaches to synthesis have been developed, including the Xerogel method [4], Pechini process [5], sol–gel method [6], sputtering [7], and coprecipitation [8]. These methods have been shown to produce powders that have narrow size distribution, and uniform composition and morphology, yielding good electrochemical performance. Nonetheless, none of these processes are continuous, and long reaction times are required.

In the past decade, spray pyrolysis, which is a continuous process, has been studied to synthesize fine $LiMn_2O_4$ powder and its derivatives, yielding materials with good electrochemical performance [9–14]. Spray pyrolysis is an aerosol process that can involve gas-, liquid-, and solid-phase reactions. The as-synthesized particles are in the nano- to micron-size range and can have a variety of morphologies. Common spray pyrolysis processes include ultrasonic spray pyrolysis [11,15], electrospray pyrolysis [9], and spray drying [12]. In the spray pyrolysis process the precursor solution is aerosolized to form fine precursor droplets. The aerosolized precursor is then introduced into a tubular furnace reactor in which the solvent evaporates, and then the precursors precipitate and decompose forming the desired product [15]. Under certain conditions, shell-structured $LiMn_2O_4$ particles are present in the products and this lowers the packing density of the material [15,16]. Spray pyrolysis requires external heating to maintain reactor temperature and this non-uniform heating can lead to non-uniformities in product, making it difficult to scale up [17,18].

Flame synthesis is a widely used technique to synthesize a number of functional powders over a range of sizes from nano- to micrometers, *e.g.,* carbon nanotubes and carbon black [19–21], metal oxide particles (TiO_2, SiO_2, Y_2O_3:Eu) [22–24], and non-oxide ceramics (Ti, TiB_2, Ta, and AlN) [25–28]. Among them, carbon black is the most successful example with daily production of about 100 tons [21]. In flame synthesis, the exothermic reaction between fuel and oxidizer generates heat to create a high temperature environment. Thus, it does not require external heating, and the heating is volumetric in flames. By changing the flame temperature and precursor solution composition, crystal structure and particle sizes

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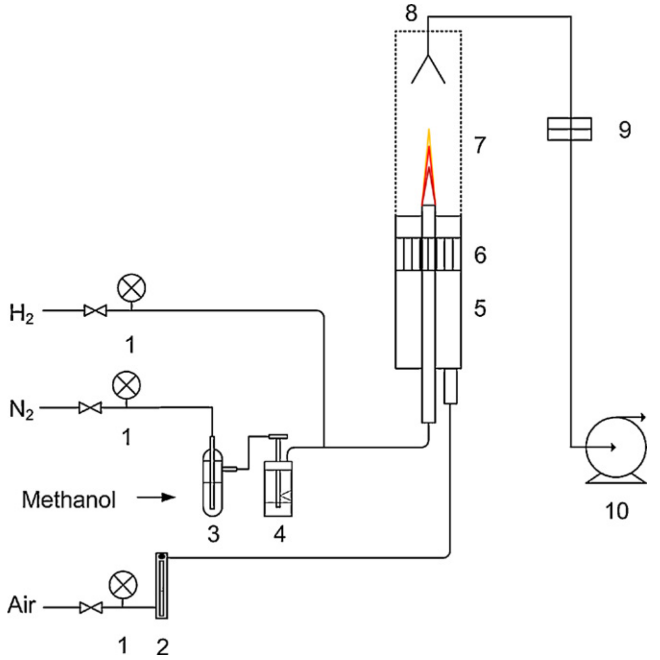

Fig. 1. Schematic diagram of the FAST setup: (1) pressure gauge, (2) flow meter, (3) methanol bubbler, (4) single-jet atomizer, (5) coflow burner, (6) honeycomb, (7) quartz chamber, (8) collection funnel, (9) filter, (10) vacuum pump.

can be varied. Hence, flame synthesis has the potential to produce cathode materials for lithium-ion batteries at a large scale and low cost.

Jang et al. have synthesized $LiCoO_2$ nanoparticles *via* flame spray pyrolysis (FSP) using H_2 as the fuel [29]. However, the electrochemical properties of the as-synthesized $LiCoO_2$ nanoparticles were not evaluated in that work. Recently, Pratsinis et al. developed an alternative FSP process to produce spinel-$LiMn_2O_4$ cathode materials using liquid-phase fuels [30,31]. In this process, metallic-organic compounds were dissolved in an organic solvent to serve as precursors. The as-produced spinel-$LiMn_2O_4$ showed a good rate capability at 4 V [32]. Nonetheless, the commercial viability of the FSP process is highly dependent on the price, availability, and compatibility of the metallic-organic precursor compounds and solvents. In the present work, a flame-assisted spray technology (FAST) is developed to produce spinel $LiMn_2O_4$ powders using low-cost metal-nitrate precursors.

2. Experimental

2.1. Powder synthesis

Fig. 1 shows a schematic diagram of the FAST experimental setup, using a hydrogen laminar-diffusion-flame to synthesize spinel $LiMn_2O_4$. The inner jet of the co-flow burner has a 10.9 mm inner diameter and is made of 316-stainless steel. A honeycomb structure surrounding the jet ensures a uniform laminar flow of air, and an open-ended cylindrical quartz chamber is used to shield the flame from the ambient environment. The precursor was prepared by dissolving stoichiometric quantities (1:2 molar ratio) of $LiNO_3$ and $Mn(NO_3)_2{\cdot}4H_2O$ in methanol. The concentrations of $LiNO_3$ and $Mn(NO_3)_2$ were 0.5 mol L^{-1} and 1.0 mol L^{-1}, respectively. The precursor aerosol was generated with a one-jet Collison atomizer (BGI Inc.) in methanol-saturated N_2 atomizing gas, where the inlet pressure was maintained at 193 kPa. The atomizing gas was saturated with methanol vapor prior to entering the atomizer to prevent evaporation of solvent methanol, thus maintaining a constant precursor concentration. The flow rates of H_2 and the atomizing gas N_2 were kept at 0.5 L min^{-1} and 2.5 L min^{-1}, respectively. The flame temperature was measured with a Pt/Rh thermocouple inserted into the flame. The data was recorded with an Omega wireless thermocouple connector. To improve the grain sizes and remove impurity phases, the flame-synthesized powder was annealed at 700 °C for 2 h. The heating rate was 10 °C min^{-1} from room temperature to 700 °C, and the cooling rate was 3.3 °C min^{-1}.

2.2. Analysis and characterization

The decomposition temperature of the precursors was evaluated *via* thermogravimetric analysis (TGA). The $LiNO_3/Mn(NO_3)_2{\cdot}4H_2O$/methanol precursor solution was isothermally heated at 50 °C for 1 h to completely evaporate the methanol solvent; then the temperature was ramped to 800 °C at 10 °C min^{-1}. Particle size distribution of the as-synthesized aerosol was measured with a scanning mobility particle sizer (SMPS) by extracting the aerosol with a glass probe at 40 cm from the burner exit. The as-synthesized powder was collected with a Nuclepore Track-etch polycarbonate membrane filter (pore size 0.2 μm) downstream of the flame. An X-ray diffractometer (Rigaku D-MAX/A) was used to acquire the crystallographic parameters and crystal structure of the powder. The scanning range was from 10° to 70° with a step size of 0.04°. The grain size of the annealed powder was calculated using the Scherrer equation from the full-width at half maximum (*fwhm*) of the (400) plane of the XRD pattern. The elemental composition of the as-synthesized powder was analyzed with an inductively-coupled-plasma mass spectrometer (ICP-MS, Agilent 7500ce). The particle morphology was examined with a scanning electron microscope (SEM, JEOL7001LVF) and transmission electron microscope (TEM, JEOL2100F).

2.3. Electrochemical performance measurement

2032 coin-type test batteries were assembled and tested with flame-synthesized powder as the cathode active materials. To prepare the cathode, a mixture of the $LiMn_2O_4$ powder, polyvinylidene fluoride (PVdF) binder and Super P conductive carbon black at a ratio of 84:10:6 by mass was suspended in *N*-methyl-2-pyrrolidene (NMP) and then homogenized to form a uniform slurry. The slurry was then cast on aluminum foil using the doctor blade technique to form a thin cathode film. The cathode film was dried in a vacuum oven at 130 °C for 16 h. To improve adhesion, the cathode was calendered to form a thin film 23 μm thick. Small, round, cathode discs (diameter 14 mm) were punched out of the dry film for the 2032 coin-type test batteries. The batteries were assembled in an argon-filled glove box. Thin Li foil (0.5 mm thick, FMC lithium) was employed as the anode and a polypropylene membrane (Celgard 2400) was used as the separator. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate solution (EC:DEC = 1:2 by weight, Ferro). The electrochemical performance of $LiMn_2O_4$ powder was tested with a MACCOR (Model 4200) battery tester. The initial charge/discharge capacity was measured between 2.5 and 4.3 V, and the cycling performance between 3.0 and 4.3 V was measured at various C-rates (charge/discharge rates). All of the electrochemical performance measurements were obtained at a constant temperature of 30 °C.

3. Results and discussion

To understand the formation mechanism of the spinel $LiMn_2O_4$ in the pyrolysis flame, the thermal properties of the precursors $LiNO_3$ and $Mn(NO_3)_2{\cdot}4H_2O$ were studied by TGA analysis. Three experiments were performed: (1) $Mn(NO_3)_2{\cdot}4H_2O$ only, (2) $LiNO_3$ only, and (3) a stoichiometric amount of $LiNO_3$ and

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