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Electrochemically active flame-made nanosized spinels: $LiMn_2O_4$, $Li_4Ti_5O_{12}$ and $LiFe_5O_8$

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Abstract

Electrochemically active $LiMn_2O_4$, $Li_4Ti_5O_{12}$, and $LiFe_5O_8$ particles with spinel structure (normal, mixed and mixed inverse) were made at production rates of 10–20 g h^{-1} by flame spray pyrolysis (FSP), a scalable, one-step, dry process. These materials were characterized by X-ray diffraction and nitrogen adsorption, and had a primary crystallite size in the range of 8–30 nm and exhibited high temperature stability. Electrochemical properties, as measured by slow cyclic voltammetry, are reported for $LiMn_2O_4$ and $Li_4Ti_5O_{12}$ as potential cathode and anode materials, respectively, in secondary lithium-ion batteries. $LiFe_5O_8$ nanoparticles were made also by FSP containing the electrochemically active β-phase as shown by the corresponding cyclic voltammogram and specific charge–discharge spectra.

Keywords: Flame spray pyrolysis (FSP); Electrochemically active materials; Nanoparticles; $LiMn_2O_4$; $Li_4Ti_5O_{12}$; $LiFe_5O_8$

1. Introduction

Nanoparticulate spinels are of growing interest in modern electrochemical applications as small dimensions reduce diffusion lengths within particles, increase the number of active sites for surface reactions and decrease the local current density [1]. Thus, when nanoparticles are used as electroactive materials in secondary batteries, the resulting overpotentials are expected to be lower and charging/discharging rates higher [2]. The control of crystallinity, particle size and morphology as well as both process productivity and cost efficiency are important for industrial applications [3].

Spinels of the type $A(B_2)X_4$ are used for a wide spectrum of applications, including electrochemistry, catalysis and electronics. In a normal spinel, the A cations occupy 1/8th of the tetrahedral sites while the B cations occupy 1/2 of the octahedral sites in the cubic closed packing formed by the anions X. In inverse spinel structures, part of the B cations occupy tetrahedral sites possibly distorting the lattice by their size. The cations may also be distributed unevenly among the octahedral and tetrahedral sites as for example in mixed spinels [4]. Moreover, it is not necessary that the A and B cations have different sizes and/or charges.

The normal spinel $LiMn_2O_4$ providing theoretically high specific energy in positive electrodes (cathodes) is potentially inexpensive and environmentally benign [5]. Ogihara et al. [6] made micron-sized $LiMn_2O_4$ particles with hard and porous microstructure by spray pyrolysis. Using a nitrate precursor solution for both Li and Mn the particles were porous, while hollow ones resulted when using acetate precursors [7]. Spinel $LiMn_2O_4$ powders with specific surface areas (SSAs) of 10–19 m^2 g^{-1} were synthesized by ultrasonic spray pyrolysis from a 0.15 M aqueous lithium nitrate and manganese acetate solution in a tubular furnace aerosol flow reactor at 1073 K [8]. Matsuda and Taniguchi [9] produced dense and hollow particles with crystallite sizes of about 17–25 nm by ultrasonic spray pyrolysis. Larger crystallites led to increased discharge capacity of about 15% at 40 cycles. Curtis et al. [10] produced $LiMn_2O_4$ nanoparticles also by wet phase chemistry with diameters from

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five to several hundred nanometer where smaller particle sizes lead to improved charge capacity and cycling performance in the 3 V discharge region if applied as electroactive cathode material.

For the anode of the lithium-ion cell, $Li_4Ti_5O_{12}$ is an attractive electroactive material [11]. This is a mixed spinel with the structure $Li(Li_{1/3}Ti_{5/3})O_4$ that has been prepared by the sol–gel method [12] and contained less than 1% anatase as the main impurity, while its SSA ranged between 53 and 183 $m^2 g^{-1}$. Commercially available $Li_4Ti_5O_{12}$ (Altair Nanomaterials Inc., Reno, Nevada, USA) with SSAs of 1.3–130 $m^2 g^{-1}$ have been tested as anode material in a lithium-ion battery by Kavan et al. [13] who found optimum performance for SSAs between 20 and 110 $m^2 g^{-1}$.

$LiFe_5O_8$ is an example of mixed inverse spinel with the structure $Fe(Li_{0.5}Fe_{1.5})O_4$. It has been proposed as a cathode material in secondary batteries and as a low-cost substitute for microwave garnets for its ferromagnetic properties [14,15]. Nanosized $LiFe_5O_8$ has been proposed for high-density magnetic recording media [16], ferrofluids [17], and other magnetic applications [18]. Conventional ceramic methods for its preparation involving high temperature sintering often lead to low SSAs and phase transitions [18]. Dey et al. [18] used a citrate precursor gel method to produce single crystallites in the 10–20 nm range through many time consuming preparation steps [15]. Whereas micron-sized particles have been investigated with rather disappointing results [19], nanosized $LiFe_5O_8$ seems promising as a cathode material in rechargeable Li-ion batteries. This has been demonstrated by Kim and Manthiram [20] and Lee et al. [21] who also synthesized their material in wet-phase processes and identified $LiFe_5O_8$ as the desired and electrochemically active phase as compared to $LiFeO_2$ [21].

Here, flame technology is used to produce electroactive nanoparticles with different spinel structures as it is a fast, dry, and versatile process for production of functional nanoparticles [22]. Laine and his colleagues [23,24] first produced monocrystalline $MgAl_2O_4$ spinel with particle sizes ranging from 25 to 50 nm by flame spray pyrolysis (FSP) of solution droplets from an ultrasonic nebulizer. In particular, FSP is a scalable process [25] allowing for production of tailor-made particles with high SSA and well-defined chemical composition [26].

This paper reports on the feasibility of controlled syntheses of nano-sized normal, inverse and mixed dense spinels for battery applications by FSP. Electrochemical testing (cyclic voltammetry) is reported for a cathode ($LiMn_2O_4$) and an anode material ($Li_4Ti_5O_{12}$). As a potential inexpensive, environmentally benign, future cathode material, the cycling performance of flame-made $LiFe_5O_8$ has also been investigated and compared to wet-phase-made $LiFe_5O_8$ reported in the literature.

2. Experimental

2.1. Powder synthesis

The experimental setup for synthesis of nanoscale powders by flame spray pyrolysis (FSP) is described in detail elsewhere [26]. Table 1 shows the employed precursors for FSP synthesis of the three spinels. These precursors were dissolved in xylene (Riedel-de-Haen, >96%, dried over molecular sieves) resulting in a certain metal ion concentration ranging from 0.5 to 1.64 M (see Table 1). Each liquid precursor solution was metered into the reactor nozzle by a syringe pump (Inotech R232) at a rate ranging from 3 to 8 mL min^{-1} and dispersed by 3 to 6 L min^{-1} oxygen (Pan Gas, >99.95%) into fine droplets by a gas-assist nozzle (pressure drop at the nozzle tip 1.5 bar). The spray was ignited and maintained by a premixed methane/oxygen flame ring surrounding the spray capillary at a radius of 6 mm (spacing was 0.15 mm) [26]. This premixed flame was fed by 1.13 L min^{-1} CH_4 and 2.40 L min^{-1} O_2. An additional oxygen sheath flow of 5 L min^{-1} was fed through a sinter metal ring (8 mm width and 9 mm inner diameter) surrounding the supporting flame to assure complete conversion of the reactants. The liquid feed and dispersion oxygen flow rates were varied to select the product particle characteristics [26]. Water cooling of the reactor prevents any precursor evaporation within the liquid feed lines or overheating of the nozzle. The gas flows were monitored by calibrated mass flow controllers (Bronkhorst). With the aid of a vacuum pump, product particles were collected on a glass fiber filter (GF/D Whatman, 257 mm in diameter) placed in a water-cooled holder 400 mm above the nozzle, keeping the off-gas temperature below 200 °C.

2.2. Material characterization

The Brunauer-Emmett-Teller (BET) specific surface area (SSA) of the powder was determined from a five point nitrogen adsorption isotherm at 77 K in the relative pressure range $p/p_0 = 0.05–0.25$ (Tristar, Micromeritics Instruments Corp.). Prior to analysis, all samples were outgassed at 150 °C for 1 h. The average primary particle diameter was calculated according to $d_{BET} = 6/(\rho \times SSA)$, where ρ is the particle density. The crystallite sizes, d_{XRD}, were determined by X-ray diffraction (XRD) patterns recorded with a Bruker AXS D8 Advance (40 kV, 40 mA) with TOPAS 2 software. The powder was also analyzed by transmission electron microscopy (TEM) with a Zeiss microscope 912 Omega with ProScan and slow scan charge-coupled device (CCD) camera at 100 kV.

2.3. Electrochemical characterization

Electrochemical characterization follows a widely applied procedure [27] as wetting of all flame-made powders was visually indistinguishable regardless of particle size: electrode sheets (thickness 350 μm) were prepared by doctor-blading FSP-made nanoparticle pastes on aluminum foil (as current collector) that was pre-treated with a carbon-based primer. After this, the electrode sheets were vacuum dried at 80 °C and then circular electrodes ($d = 13$ mm) were punched out with an approximate weight of 3 mg of the electroactive spinel. The pastes containing 300 mg of FSP-made $LiMn_2O_4$ or $Li_4Ti_5O_{12}$ were mixed with 300 mg carbon black (Printex 90, Degussa) and 12 mg of polyvinylidene fluoride (SOLEF PVDF 1015, Solvay) for 5 min and dispersed with 4 g of a

Table 1
Precursor solution composition and metal ion molarity for powder production by FSP

Sample	Molarity (M)	Precursor
$LiMn_2O_4$	0.6	1.0 M solution of Li-*t*-butoxide in tetrahydrofuran (Aldrich), Mn(III)-acetylacetonate (Aldrich)
	0.6–1.8	1.0 M solution of Li-*t*-butoxide in tetrahydrofuran (Aldrich), Mn-2-ethyl-hexanoate (Strem Chemicals)
$Li_4Ti_5O_{12}$	0.82–1.64	1.5 M solution of Li-*t*-butoxide (Strem Chemicals) in tetrahydrofuran (J.T. Baker, >99%), Ti-isopropoxide (Merck, >98%)
$LiFe_5O_8$	0.05	1.0 M solution of Li-*t*-butoxide in tetrahydrofuran (Aldrich), 80% Fe-naphtenate in mineral spirits (Strem Chemicals)

Xylene is used as solvent in all solutions.