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Flame co-synthesis of $LiMn_2O_4$ and carbon nanocomposites for high power batteries

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ABSTRACT

A novel method to produce $LiMn_2O_4$/carbon nanocomposites in a rapid, one-step and industrially scalable process is presented. A flame spray and a diffusion flame are combined to continuously produce $LiMn_2O_4$ nanoparticles and carbon black, respectively. Powder carbon content is varied by adjusting the diffusion flame conditions. The powders are characterized by X-ray diffraction (XRD), transmission electron microscopy, cyclic voltammetry and galvanostatic cycling for a range of current densities. These $LiMn_2O_4$/carbon nanocomposites retain over 80% of their initial galvanostatic discharge capacity for current densities ranging from 5 to 50C-rates, significantly better than pure $LiMn_2O_4$ nanoparticles mixed conventionally with commercial carbon blacks. The improved performance of the $LiMn_2O_4$/carbon nanocomposites is attributed to the carbon particle contact and/or film coating of the freshly-made $LiMn_2O_4$ nanoparticles. This additional well-distributed carbon provides an electrically conductive network that induces a more homogeneous charge transfer throughout the electrode. The suitability of these nanocomposites as a hybrid material is discussed by considering the layout of a thin-layer lithium-ion battery containing these flame-made nanocomposites as positive electrode and LiC_6 as negative electrode. The battery's specific energy is calculated to be 78 Wh kg^{-1} (50C-rate) based on the results of lithium-ion insertion capacity experiments and reasonable engineering assumptions on the lithium-ion battery design.

1. Introduction

One leading alternative cathode material to $LiCoO_2$ is $LiMn_2O_4$ for its lower cost, higher electrochemical potential vs. graphite, and its improved thermal stability [1–3]. High power applications such as electric vehicles require that lithium-ion batteries have a high specific power and energy [4,5]. One route to increase specific power is to significantly increase the interfacial area between electrochemically active material and electrolyte, thereby increasing the charge and discharge rates [6]. This opportunity has led many groups to develop nano-structured and/or nano-sized $LiMn_2O_4$ particles [7–10] and with promising results.

The full charge capacity of nano-sized cathode and anode materials cannot be realized if local electrical conductivity is insufficient for the given power demand. In other words, if an electrically conductive filler is not well dispersed throughout the active material, there will be parts of the active material which do not contribute to the capacity when a constant, high current is required. Therefore, sufficient dispersion of the electrically conductive additive amongst the active material is necessary for effective use. Carbon black (CB) is used commercially as an electrically conductive additive, either as a coating of the active material or as a powder dispersed throughout the active material. It is produced industrially by incomplete combustion of a gaseous or liquid hydrocarbon [11]. The lack of oxygen limits CO_2 formation and promotes CO, H_2 and carbon–carbon bond formation, contributing to the elemental carbon structure of CB.

Flame technology is used for CB production but is not a typical method for lithium-ion cathode material production. Our group has recently introduced flame spray pyrolysis (FSP) as a route to producing LiV_3O_8 [12] and $LiMn_2O_4$ nanoparticles [10] for use in lithium-ion batteries. Carbon-coated nanoparticles have been made by single flame combustion of $SiCl_4$ and acetylene [13] or hexamethyledisiloxane and H_2 [14] at production rates up to 700 g h^{-1}. Carbon-coated TiO_2 with or without soot (or CB) particles were made at high or low acetylene concentrations [15] in vapor-fed flames. Strobel et al. [16] made NO_x-storage reduction catalyst particles by two spray (liquid-fed) flame synthesis of separate Al_2O_3

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and Pt/BaO or $Pt/BaCO_3$ nanoparticles. Ernst et al. have recently used flame technology for synthesis of platinum clusters embedded in CB by a one-step process [17]. They have also made Pt-clusters supported on CB by two separately staged spray flames: the first flame produced the CB particles while a second one downstream produced the Pt clusters that were scavenged onto the surface of the earlier formed co-flowing CB particles [17].

Vapor- and liquid-fed flame technology [15,17] is combined here to simultaneously make in one-step, for the first time to our knowledge, $LiMn_2O_4$/carbon nanocomposites for positive electrodes in lithium-ion batteries. Here, flame co-synthesis of $LiMn_2O_4$/carbon is presented and the electrochemical charge capacity of these materials at various specific currents (also known as C-rates) is shown. A description of the experimental method is given and an outlook of the benefits and challenges of this one-step synthesis of cathode material and its simultaneous carbon coating is presented.

2. Experimental

The precursor for synthesis of $LiMn_2O_4$ nanoparticles was prepared by mixing a 1:2 molar ratio of Li:Mn in an organic, combustible solution. More specifically, 4.5 g of Li–acetylacetonate (Aldrich) and 30.2 g of Mn(III)–acetylacetonate (Aldrich) were dissolved into 160 mL of 2-ethylhexanoic acid (Riedel-de Haën) and then 160 mL of Acetonitrile (Sigma–Aldrich, 99.5%) was added [10]. To ensure complete dissolution of the acetylacetonates, the solution was heated to 160 °C for 2 h while connected to a cooling reflux to ensure no mass loss.

The experimental set-up of FSP is described in detail elsewhere [18]. The liquid precursor was sprayed at a rate of 3 mL min^{-1} and dispersed by 5 L min^{-1} of oxygen. The spray was ignited by a support flame created by 1 L min^{-1} of methane and 3 L min^{-1} of oxygen. A pressure of 1.5 bar was maintained across the nozzle tip during synthesis. The spray flame (SF) nozzle was cooled by water to prevent overheating and precursor evaporation within the liquid feed lines. The carbon black was produced by supplying acetylene gas to the diffusion flame (DF) [13,17] using still air as oxidant prior to ignition of the flame spray. Hereafter, the diffusion flame-made carbon black produced in this work is referred to as DF–CB.

Four powders were produced: one with only $LiMn_2O_4$, two with varying $LiMn_2O_4$ and carbon content, and one with only DF–CB. The acetylene gas was supplied for production of these powders at 0, 0.5, 1.0, and 0.6 L min^{-1}, respectively. A schematic of the experimental set-up is shown in Fig. 1. Note that the distances and angle between the nozzles are provided.

Particles were collected on a glass-fiber filter (GF/D Whatman, 257 mm in diameter) placed 0.5 m directly over the flame or flames using a vacuum pump (Busch, Seco SV 1025). The Brunauer-Emmett-Teller (BET) specific surface area (SSA) of these powders was determined through a five-point nitrogen adsorption isotherm at 77 K (Tristar, Micrometrics Instruments Corp.) after degassing the samples with nitrogen at 150 °C for 90 minutes. The X-ray diffraction (XRD) measurements were performed using a Bruker AXS D8 Advance (40 kV, 40 mA) and analyzed with the Topas 2 software. The XRD measurement was performed at a continuous scan between 2θ angles of 10° and 70° at a scan rate of 0.03° min^{-1}. For the investigation by transmission electron microscopy (TEM), the material was deposited onto a holey carbon foil supported on a copper grid (Okenshoji Co., Ltd.). TEM investigations were performed using a CM30ST microscope (Philips; LaB_6 cathode, operated at 300 kV, point resolution ~2 Å).

The carbon content in the powders was measured thermogravimetrically in an oxidizing environment. Powder samples were heated up at a rate of 10 °C min^{-1} from room temperature up to 800 °C under 50 mL min^{-1} of air with the powder mass change

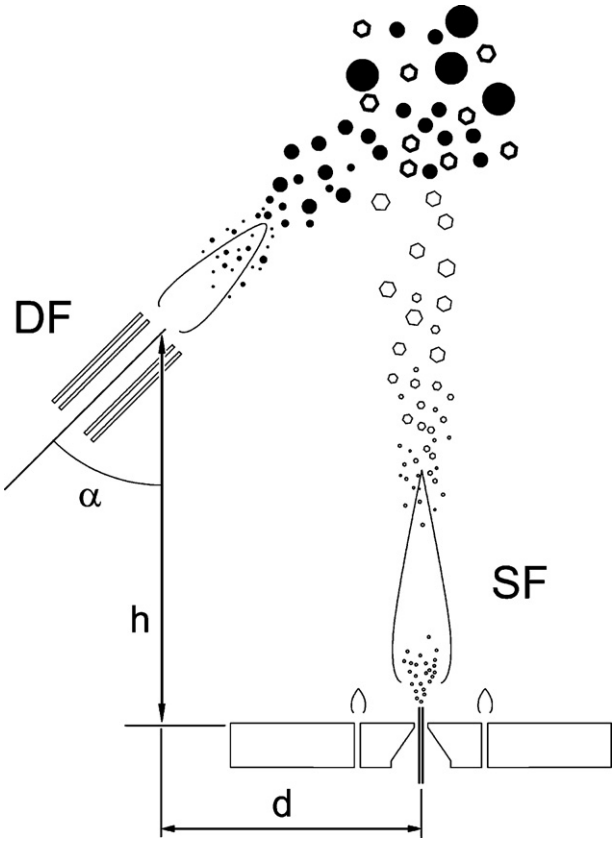

Fig. 1. Schematic of the co-synthesis of carbon black (DF–CB) and $LiMn_2O_4$ nanoparticles by a diffusion flame (DF) and a spray flame (SF), respectively. The distance between the nozzle tips are d = 5 cm and h = 9 cm. The angle between the nozzle axes is α = 45°.

measured via the Mettler Toledo TGA/SDTA851^e thermobalance. Electrodes made from the flame-produced powders, Super P (commercial CB, TIMCAL SA, BET SSA = 62 m^2 g^{-1}), and polyvinylidene fluoride (PVDF SOLEF 1015, Solvay) had a mass ratio of 7:2:1, respectively. They were prepared by first dispersing the flame-produced powder with the Super P in *N*-methylpyrrolidinone (NMP, Fluka) solvent. A solution of 10 wt.% PVDF dissolved in NMP was then mixed into the suspension to form a viscous slurry. The slurry is spread by doctor-blading at a thickness of 200 μm onto an aluminum foil and dried under vacuum at 110 °C overnight in order to remove the solvent and form a composite electrode.

Electrodes with a diameter of 13 mm were punched out and dried in a vacuum chamber at 120 °C overnight. They were then assembled in test cells similar to coin cells [19] where they function as working electrodes. Lithium metal (Aldrich, 99.9%) served as both counter and reference electrode. It was separated from the working electrode by a 1 mm thick fiberglass separator soaked in 500 μL of electrolyte [1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by mass), Ferro GmbH]. Cells were assembled in an argon-filled glove box with less than 1 ppm of oxygen, water, and nitrogen contents.

Both cyclic voltammetry (CV) and galvanostatic measurements were performed by a computer-controlled cell capture (CCCC) system (Astrol Electronics AG, Oberrohrdorf, Switzerland) at 3.0–4.5 V vs. Li/Li^+ at a potential scan rate of 0.1 mV s^{-1}. For the rate capability experiments, the electrodes were cycled galvanostatically in the range of 3.5–4.3 V vs. Li/Li^+ for varying specific currents proportional to the mass of $LiMn_2O_4$. To quantify the contribution of the DF–CB's capacity, electrodes of DF–CB and PVDF were cycled and the capacity measured. The contribution