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An innovative method to observe rate capability of Li-ion battery composed of spinel cathode material

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ABSTRACT

An innovative method is developed to measure specific surface areas (SSAs) of a battery's cathode active material from its particle size distribution and XRD measurements and its applications to observe and monitor the rate-capability behavior of the lithium ion battery. This method is applied on Li-ion batteries of spinel cathode material and its validity is discussed based on the measured capacities of the fabricated batteries and comparison of the calculated SSAs with those measured experimentally. The present method predicts the processing effect on battery performance and is thought to be time-saving in optimizing the processing parameters of the cathode material. It can also be extended to other systems of spinel structures thus assisting, in general, the development of lithium ion batteries.

1. Introduction

Spinel structures of lithiated transition metals oxides are attractive materials for rechargeable batteries in versatile energy storage technologies and applications because they have moderate capacity with high voltage plateaus and relatively high energy density in addition to low cost [1–4]. Achieving, simultaneously, desirable values of capacity, cycleability and rate performance is a challenging task which requires a good understanding of the electrochemical reactions occurring in the electrodes active materials and the influencing parameters such as composition, morphology, structure and size [5]. Particle size is one important parameter in developing cathode compounds because it affects the battery cycleability and performance [6]. However, there seems to be a disagreement on size effects in different size ranges i.e., in the micro-scale and nano-scale [7]. In some cases, reducing the particle size of some compounds can even alter their insulating nature to electroactive due to shortening of diffusion distances of lithium in nanoparticles leading to high rate capability. In other cases the increase of surface area due to size reduction may aggravate any tendency toward irreversible reaction with the electrolyte leading to undesirable performance of the battery [8–11]. It may also impact practical issues due to difficult processing into the electrodes and the necessity to add more carbon to the composite cathode to ensure good electrical connectivity which affects other properties like energy density and weight. Therefore, reducing particle size should be approached with caution. In this view, particle size and surface area are key parameters in maximizing rate capability and optimizing battery performance. Reducing and controlling particles sizes may involve costly and complex procedures starting from synthesis to processing of the electrodes compounds [12–16]. Milling is the simplest method for size reduction which, at the same time, guarantees purity of the processed powders. However, it may generate sizes of wide distributions or affect the stoichiometry of the powders. It is therefore the aim of this work to shed more light on the effect of size reduction on the battery performance using an innovative method correlating the battery attainable capacity to the specific surface area of its cathode active material which is determined from size distribution and XRD measurements. Furthermore, since the exploration of materials for Li ion batteries usually follows the thread of synthesis-characterization-test-analysis, which is a time consuming and costly process, the present method is thought to be direct and time-saving for optimizing the processing parameters of the cathode active compounds.

2. Materials and methods

The stoichiometry of the targeted material is in the form $Li_{1+y}Mn_{2-y-z}Fe_zO_4$, where $y \leq 0.03, z \leq 0.05$. The details of the synthesis of the active material by a sol–gel method were reported earlier (see reference [17]). The as-synthesized material was calcined in air at 850 °C for 24 h. The compound powders were divided into three groups, two of which were processed in a ball mill machine

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(Planetary Micro Mill PULVERISETTE 7 premium line) from FRITSCH for 5 and 10 h at 600 rpm using 10 balls 4 g each. The grinding bowl and balls are all made of ZrO_2. The synthesized materials were heated to 200 °C for 24 h prior to each milling process, which was then performed in a dry medium for intervals of 5 min run to 5 min rest to avoid possible phase alteration due to the heat generated from the milling process [18]. The three powders, thereafter labeled P1, P2 and P3, refer to cathode materials underwent ball-milling for 0, 5 and 10 h respectively. The particle size distributions of the powders were measured by a Malvern Mastersizer Range particle size analyzer. For every powder a precise amount of the material was dispersed in 1 ml of distilled water, and sonicated for 10 min. Measurements were repeated to ensure consistency of results. The powders morphologies were photographed using JEOL JSM-6700F a field emission scanning electron microscope. The XRD measurements were performed using PANalytical X'pert Pro MDP instrument with a real-time multiple strip (RTMS)-type detector (X'celerator), spinning holder, and the reflection-parafocusing geometry of Bragg–Brentano. The XRD spectra were measured with a step time and step size appropriate for refinement and quantitative analysis which was carried out using the X'pert High Score Plus software. The specific surface areas of the processed powders were measured experimentally using nitrogen gas adsorption based on Brunauer, Emmett and Teller (BET) method [19]. The measurements were achieved using ASAP 2020 V3.04G instrument from Micromeritics. All cathodes were fabricated from a mixture of 81.4% of the active material, 9.7% of activated carbon and 8.8% of polyvinylidine fluoride (PVDF) binder and pasted on metallic mesh as a current collector. The assembled cells were composed of a positive electrode, a porous polypropylene separator (Celgard 2500) and a Li foil anode all immersed in 1 M of lithium hexaflurophosphate ($LiPF_6$) electrolyte in 1:1 volume ratio of ethylene carbonate (EC) and dimethylcarbonate (DMC). The fabricated batteries were operated and tested using a 16-channels automatic battery cycler (WBCS3000) from WonaTech Instrumentation. The charge/discharge cycling characteristics were investigated in the voltage range 4.2–3.0 V at 1 mA current and room temperature.

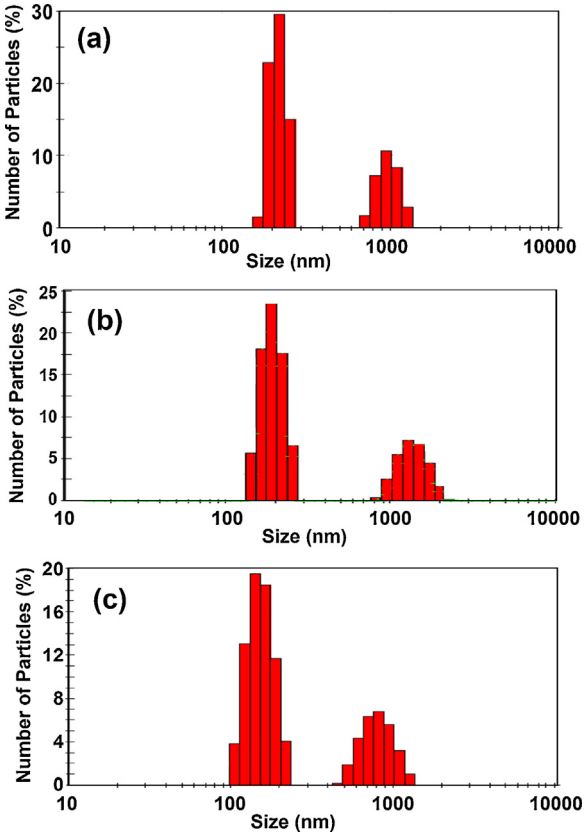

Fig. 1. The particle size distributions of the cathode active material. (a) Unprocessed powder, (b) milled for 5 h and (c) milled for 10 h.

3. Results and discussion

Fig. 1(a–c) shows the particle size distributions of the P1, P2 and P3 powders. Two major populations were observed in the

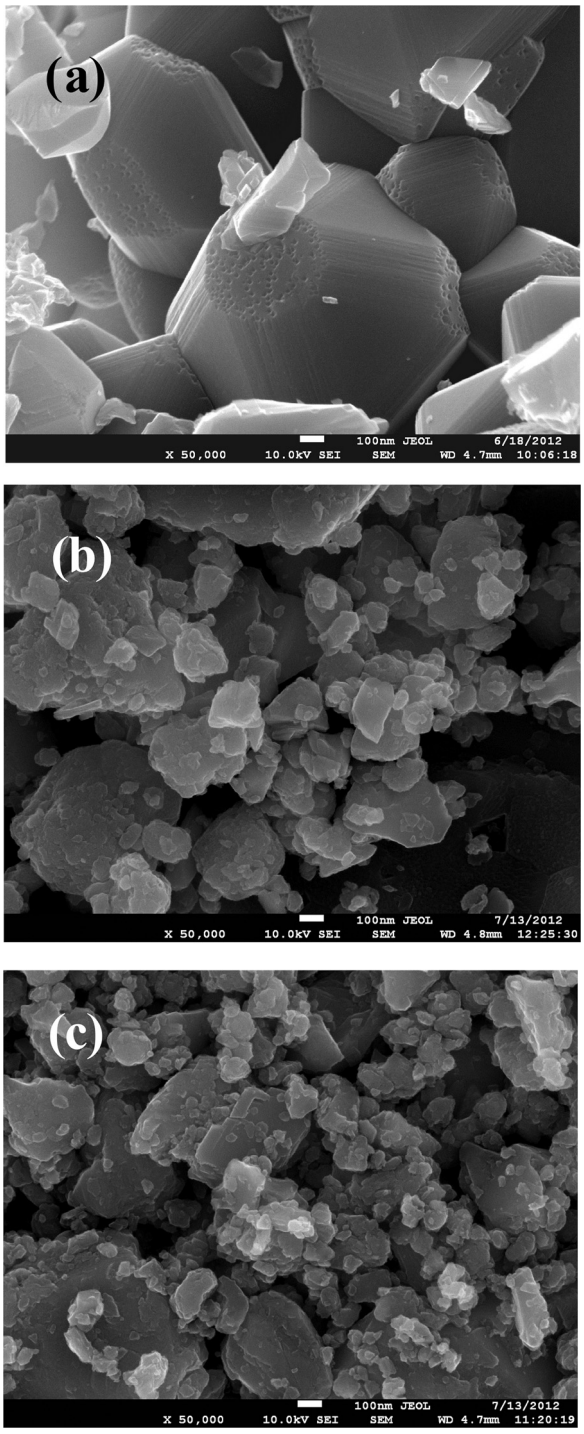

Fig. 2. Morphologies of the cathode powders under scanning electron microscope for (a) P1 powder (unprocessed by ball mill) (b) P2 powder (after 5 h ball mill) (c) P3 powder (after 10 h ball mill).