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Original Research Paper

Optimization of $LiFePO_4$ wet media milling and regressive population balance modeling

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A B S T R A C T

$LiFePO_4$ (LFP) is a low cost cathode material for Li-based batteries, but its low intrinsic ionic and electronic conductivity require sub micron particles to achieve acceptable energy capacity and charge and discharge rates for automotive applications. Consequently, for top-down syntheses, grinding energy and throughput are critical to maintain its cost advantage versus alternative processes and materials. Here, we demonstrate that an aqueous media mill reduces LFP powder from 27 μm (d_{50}) to 0.2 μm. We applied a Taguchi experimental design to assess the effect of LFP loading (0.20–0.30), yttria-stabilized zirconia media (YSZ) size (0.3–0.5 mm), surfactant-to-LFP mass ratio (0–0.008), and mill rotation rate (40–80 Hz) on specific throughput and effective grinding energy. The 0.3 mm YSZ media reduced the LFP powder at a specific throughput of 0.40 $kg_{LFP}/kg_{media}/h$ at an LFP loading of 0.30 (mass fraction of LFP to suspension), a surfactant-to-LFP mass ratio of 0.008 and a mill rotation rate of 60 Hz. Under these conditions, the effective grinding energy was 0.32 kW h/kg_{LFP}.

The Austin II Population Balance Model characterizes the change in particle size distribution with time: the deviation between the model and the experimental data was 0.026 μm for each of the particle fractions d_{10}, d_{50} and d_{90}. This empirical model describes throughput at any given target particle size at the optimum operating condition.

1. Introduction

The lithium ion battery (LIB) market continues to grow as countries seek to electrify transport and energy storage to meet environmental constraints [1]. Few cathode battery materials are available that adequately meet all battery performance metrics [2]. Moreover, LIB cost remains high for electric vehicles or renewable energy storage [3]. $LiCoO_2$ cathodes have excellent performance but are more hazardous than compositions with iron. Padhi et al. [4] proposed $LiFePO_4$ (LFP), also known as triphylite (Fig. 1), as a cathode material, which has better thermal stability and a high theoretical specific capacity ($170\ mA\,h\,g^{-1}$), which makes it a low cost option compared to $LiCoO_2$ or $LiMn_2O_4$. On the other hand, the intrinsically low ionic and electronic conductivity of LFP leads to high polarization, poor rate capability [5,6] and low discharge capacity [7]. Reducing the particle size addresses these shortcomings. However, the tap density is lower, which requires more carbon binder, reduces the specific energy [8] and increases the manufacturing complexity [9].

Discharge capacity is greatest for particles in the range of 0.1–0.2 μm [10,11]. Also, the electronic performance of LFP with narrow particle size distribution (PSD) from 0.1 μm to 0.2 μm is better than a wider distribution [12].

Gauthier et al. invented a melt-cast process to synthesize [13,14], which has the potential to reduce the reactant cost several fold. However, it requires several particle reduction steps—jaw crushing, roller milling, jet milling/media milling—to achieve submicron particles from large ingots. Wet media milling followed by spray drying and carbon coating are standard operations to produce cathode material for Li-ion batteries. Wet media milling can reduce the PSD below 0.1 μm [15]. The spray dryer evaporates most of the solvent and water and forms small agglomerates that are subsequently treated in rotary kilns at high temperature to coat the surface with carbon. Residual moisture and organic compounds evaporate or react during this process. In wet media milling, water and LFP form a slurry that circulates through the chamber and mixing tank. A motor rotates impellers in the milling chamber charged with grinding media (Yittria-Stabilized-Zirconia YSZ) that fractures and abrades the LFP as they collide [16] (Fig. 1).

Attrition rates depends on solids loading [17], impeller rotation rate, liquid type, media, time, slurry circulation rate, slurry

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Symbols

a	coefficients
$b_{i,j}$	specific breakage rate parameter (dimensionless)
$B_{i,j}$	cumulative breakage rate parameter (dimensionless)
B	cumulative Breakage function matrix
CAPEX	capital expenditures
$d_p(i)$	particle size for class i (μm)
E	effective grinding energy (kW h/kg_{LFP})
FE–SEM	field emission scanning electron microscope
h_{ij}	element of lower triangular matrix
H	lower triangular matrix
J_{ij}	element of diagonal matrix
J	diagonal matrix
L	LFP loading (mass of LFP/mass of suspension)
LFP	$LiFePO_4$
LIB	lithium ion battery
M	media size (mm)
N	total number of size classes
OPEX	operating expenditures
PBM	population balance modeling
PSD	particle size distribution
Q	specific throughput ($kg_{LFP}/kg_{YSZ}/h$)
R	rotation rate (Hz)
S_i	selection parameter in size class i (min^{-1})
$\mathbf{S}$	select function vector
T	surfactant-to-solid mass ratio
t	time
TEM	transmission electron microscope
v_i	volume parameter in size class i (dimensionless)
$\mathbf{v}$	specific volume fraction matrix
$\mathbf{V}$	cumulative volume fraction matrix
YSZ	yttria-stabilized-zirconia

viscosity, impeller tip velocity, and chamber size [18–20]. Surfactants lubricate the slurry to increase milling efficiency by increasing particle dispersion, and reducing agglomeration. Consequently, milling more concentrated slurries is possible [15,21]. We tested Tween-20, Triton ® X-100, Igepal ® CA-630, Docusate (Dioctyl sulfosuccinate sodium salt, 96%). The Tween-20 foamed less and required lower concentrations to achieve higher slurry concentrations. Furthermore, since it is an organic surfactant, it does not contaminate the LFP as it evaporates or reacts during the carbon coating process.

Here we report the effect of LFP loading, impeller rotation rate, media size and surfactant-to-LFP mass ratio on wet milling performance. We show that the Population Balance Modeling (PBM) characterizes the change in the PSD with time.

2. Material and methods

The LFP source material comes from 50kg melt-casted ingots [14]. A Pulverisette 1 model II, Fritzch jaw crusher reduced that ingots size to 1–3 mm then a 4-stage roller grinder (MPE Chicago) further reduced it to a d_{50} of 27 μm and a d_{99} of 200 μm as measured by Horiba LA-950. We operated a Minifer mill (NETZSCH - Feinmahltechnik GmbH), with a 100 μm mesh filter and loaded 120 mL YSZ media, and filled the chamber to 60% of the total volume. The mixing tank contained 292 mL of water and Tween-20 surfactant. After milling, a spray dryer evaporated the water from the slurry and then the powder was coated with carbon. The surfactant evaporated with the water and residual organics reacted to form carbon during the coating process. Thus far, low concentrations of YSZ ($Zr < 500$ ppm) from wear of the grinding media has had an inconsequential affect of battery performance. Commercial grinding chambers are made of ceramic rather than stainless steel to minimize Fe contamination.

The Netzsch minifer pumped cold water around the grinding chamber at a rate sufficiently high to maintain the slurry effluent at 25 °C (Fig. 2). The particles circulate from the chamber to the mixing tank at a frequency of 0.5 min. We sampled the slurry at the exit of the grinding chamber that represented the instantaneous PSD in the system—that is, we consider it to be fully back-mixed. LFP is progressively added at a rate slow enough to ensure the filters remained clear. Time ’0’ represented the point at which we first introduceed LFP to the mixing tank. We extracted samples at 5–15 min^{-1} intervals to measure the PSD. For each test, we added 1 or 2 droplets of the LFP slurry to the sample bath immediately after withdrawing it. We set the refractive index of LFP to 1.6800 for the real part and 0.1 for the imaginary part, and for the distilled water we set the real part to 1.3333 and 0 for the imaginary part. The instrument precision is within 10%

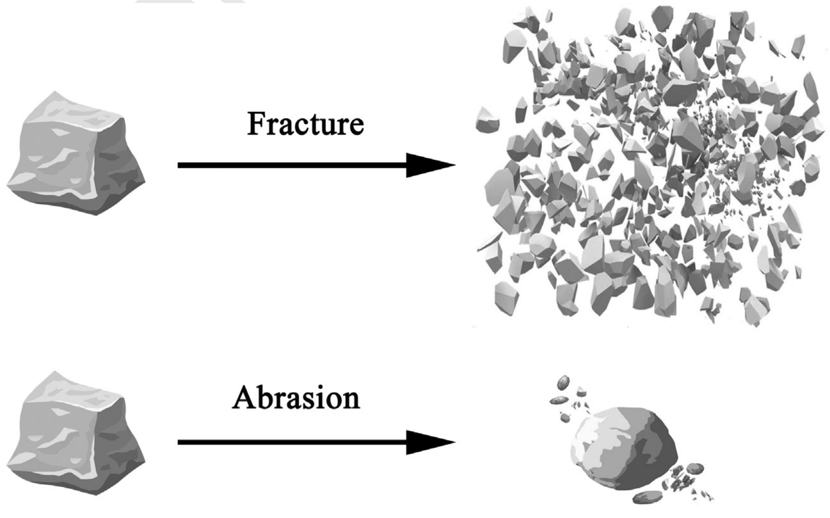

Fig. 1. Fragmentation mechanisms.

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