Tuning solution chemistry for morphology control of lithium-ion battery precursor particles

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ABSTRACT

Many battery materials are synthesized via calcination of precursor particle powders with a lithium source. The precursor particles frequently are made via coprecipitation reactions, and a number of combinations of coprecipitation agents have been demonstrated previously. Detailed control over the morphology of precursor particles and the resulting final electrode materials would be highly desirable, but currently detailed understanding of the impact of synthesis conditions on precursor morphology are lacking. Herein, tunable monodisperse $MnCO_3$ particles for Li-ion battery precursors of varying size and shape were synthesized through batch coprecipitation. The effect of solution chemistry on final particle morphology was confirmed via scanning electron microscopy and considered in the context of solution equilibrium calculations and nucleation and growth of precipitate crystals. The tunability of $MnCO_3$ particle morphology with reagent concentration was demonstrated with transitions from rhombohedra to cubes to spheres to smaller spheres with regards to overall secondary particle structures. Other experimental factors were also examined to further understand the processes resulting in the transitions in $MnCO_3$ morphology. Precursor particles were calcined to form $LiMn_2O_4$ to verify the ability to maintain the tunable morphology in the final battery materials and to confirm suitability for battery cathodes.

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1. Introduction

Lithium-ion batteries have become the dominant technology for consumer electronics applications and are increasingly being developed for larger-scale applications such as electric vehicle batteries and stationary energy storage [1]. While historically, battery progress has largely been tracked by adoption of chemistries and materials structures with higher energy densities [2–4], another important factor in battery performance is the morphology of the electrochemically active particles within the battery electrode as well as their organization and distribution within the composite structure. For example, the battery materials literature is full of the synthesis and characterization of materials with a wide variety of particle shapes and sizes, including rods [5,6], cubes [7], spheres [8,9], urchins [10], plates [11], and many others [12–15]. In some cases, the morphology serves to provide preferential diffusion paths for lithium or conduction paths for electrons that improve rate capability or energy density of the battery material [11]. In other reports, the morphology is taken advantage of to organize the overall electrode structure to accommodate improvements in lithium-ion diffusion in and out of the electrode as a whole [16]. One of the key factors in being able to take advantage of active particle morphology-dependent improvements in battery electrode performance is that the electrode

particle morphology must be well-controlled [17]. Thus, underlying mechanisms that result in the final particle morphology with regards to size, shape, porosity, surface roughness, and polydispersity are important to engineering particles for battery electrodes. In addition, tunability of one or more of these morphology metrics would also be desirable. The study described herein focuses on efforts to control particle morphology in a battery electrode precursor particle system.

The chemistry employed to synthesize precursor particles in this study was coprecipitation of Mn^{2+} with carbonate salts to form $MnCO_3$. Coprecipitation was chosen as a method because it is highly tunable and easily scalable for particle synthesis [9,18–22] and $MnCO_3$ was chosen as a target precursor chemistry because it can be calcined with a lithium source to form the final battery material $LiMn_2O_4$ [23]. Given the relatively lower complexity of only having one transition metal involved in the coprecipitation synthesis and the availability of data on $LiMn_2O_4$ in the battery literature [24–27], $MnCO_3$ serves as a model system for precursor morphology tunability. A number of reports have previously been published in the literature on synthesis of transition metal carbonates, including $MnCO_3$, and a variety of particle morphologies that may be achieved [13,28–31]. Notably, the most commonly reported morphology for transition metal carbonates used for battery material templates is approximately spherical and has relatively high polydispersity [13,32,33]. The extent of the tunability of the morphologies and polydispersity of transition metal carbonate template particles, however, is currently unknown. The ability to be predictive

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in the resultant morphology of these particles would in principle enable detailed studies of the influence of particle morphologies on lithium-ion battery performance.

In general, the morphology of particles generated from coprecipitation reactions can be influenced by a variety of factors, including reagent concentrations, nucleation and growth rates, ripening, collisions with reactor walls and other particles, temperature, and chemical modifiers including chelating agents [18,34,19]. Due to the high level of complexity for consideration of all of these factors, we have focused our initial study on the influence of solution chemistry on particle morphology. In this paper, we will demonstrate a variety of particle morphologies that are accessible via relatively modest changes in coprecipitation solution chemistry. These morphologies are likely not driven by ripening processes that have been demonstrated to influence morphologies for other coprecipitation processes for battery particles previously reported in the literature for hydroxide synthesis [34]. The conversion of our precursor particles to lithiated battery electrode active materials was also performed to demonstrate that the tunable morphologies can be retained in the resulting final electrode materials. While our solution chemistry approach is an initial report of understanding the morphology tunability of this battery precursor system, we speculate a wide design space of size, shape, and surface roughness control will be accessible via detailed study of this synthesis platform.

2. Experimental

2.1. Preparation of $MnCO_3$ and $LiMn_2O_4$ particles

$MnCO_3$ particles were prepared as follows: 1200 mL of 1.5–240 mM NH_4HCO_3 (Fischer) in deionized (DI) water was poured all at once into 1200 mL of 1.5–12 mM $MnSO_4 \cdot H_2O$ (Fischer) in DI water solution in a 4 L beaker. Solutions were preheated to 50 °C prior to mixing and the temperature was maintained at 50 °C for the duration of the synthesis. The solution was stirred gently with an impeller at 500 rpm to prevent particle settling in solution and $MnCO_3$ particles were precipitated for 0.5 h. All syntheses were done at a pH of ~7.5. Vacuum filtration was used to collect the particles, and the particle cake was rinsed with 2 L DI water before being vacuum dried at 80 °C overnight. $MnCO_3$ particles were converted to $LiMn_2O_4$ particles through calcination after mixing stoichiometric quantities of LiOH in a Carbolite CWF 1300 box furnace in an air atmosphere at 800 °C for 5 h.

2.2. Material characterization

Powder X-ray diffraction was performed with a PANalytical X'Pert Pro MPD using CuKα radiation. Scanning electron microscopy (SEM) with an FEI Quanta 650 SEM was used to image all samples. Particle size distributions were obtained by analysis of SEM images with the program ImageJ [35].

2.3. Electrochemical characterization

Electrochemical analysis was done using CR2032 coin cells with lithium metal anodes and cathodes containing the synthesized $LiMn_2O_4$ active material. The $LiMn_2O_4$-containing cathode was prepared by coating a slurry composed of $LiMn_2O_4$ active material, carbon black conductive additive, and polyvinylidene diflouride binder in a weight ratio of 80:10:10 onto an aluminum current collector. The electrode slurry was dried in an 80 °C oven overnight and dried in an 80 °C vacuum oven for 3 h prior to punching out 14 mm electrode disks. The electrolyte used was 1.2 M $LiPF_6$ dissolved in a solution containing 3:7 ethylene carbonate:ethyl methyl carbonate. Cells were cycled between a voltage window of 3.4–4.2 V vs Li/Li$^+$ using a MACCOR battery tester.

3. Results and discussion

In this study, we specifically focused on the influence of solution chemistry on $MnCO_3$ particle morphology. We designed our experiments to systematically vary both the total Mn^{2+} initially in solution (via total amount of $MnSO_4$ salt originally dissolved in DI water) as well as the ratio of the dissolved transition metal to the coprecipitation agent. In our case, coprecipitation was facilitated by the CO_3^{2-} from dissolved NH_4HCO_3.

A representative example of the dramatic changes in $MnCO_3$ particle morphology facilitated by changes in total initial Mn^{2+} concentration (with constant NH_4HCO_3:$MnSO_4$ ratio of 40:1) can be found in the SEMs in Fig. 1. At the lowest initial Mn^{2+} concentration (1.5 mM), particles were relatively large at just under 10 μm in average length of a particle side (Fig. 1A). The particle surfaces appeared smooth and the overall shape was rhombohedral, with the wide angle measured to be ~103° from SEM images. It should be noted that this was similar to the rhombohedral angles reported for single $MnCO_3$ crystals [36]. We also note that these particles have a large degree of clustering relative to others from the synthesis series shown in Fig. 1, with particles often fused together. A slight increase in concentration from 1.5 to 3 mM initial Mn^{2+} resulted in a transition from a rhombohedral morphology to a cubical morphology (Fig. 1B). The cubical particles were approximately the same size and the surfaces were smooth; however, all angles on the particles were now ~90°, and it was rare to find the cubical particles attached or clustered together. An increase in Mn^{2+} concentration to 4.5 mM resulted in particles that are in a transition region between cubical and spherical particles (Fig. 1C). The average particle size (an approximate diameter assuming they were spherical) is not significantly different from the rhombohedra or cubes; however, there were many edges and corners on the surfaces of the particles and there was a flaky, layered appearance to the surface resulting in a large degree of surface roughness. There was no longer an obvious 8 sharp corners on the particle surface. At 6 mM Mn^{2+}, the resulting particles have transitioned to an approximately spherical morphology (Fig. 1D). The diameters of the spherical particles were on approximately the same length scale as the particle length/diameters of the previously collected particles at lower Mn^{2+} concentrations. It was clear the overall spherical secondary particle morphology consisted of aggregates of smaller faceted particles that can be seen at the surfaces of the particles. A further increase in Mn^{2+} initial concentration to 7.5 mM resulted in spherical particles as well (Fig. 1E). These particles were also clearly made up of smaller primary particle aggregates that have agglomerated into a secondary structure that was approximately spherical. Relative to the spherical particles at the slightly lower Mn^{2+} concentration (Fig. 1D), the average particle size has dropped significantly with the diameters decreasing by almost a factor of 4 (Fig. 1E). Subsequent increases in initial Mn^{2+} concentration to 9 mM (Fig. 1F) and 10.5 mM (Fig. 1G) resulted in particle morphologies that were approximately spherical and similar to those found at 7.5 mM (Fig. 1E), although as the Mn^{2+} concentration was increased, the average diameter of the particles decreased slightly. We note that a final synthesis was done at 12 mM initial Mn^{2+} concentration; however, the particles were not recoverable for SEM characterization. A cartoon illustrating the transition from rhombohedral to cubical to transitionary cubical/spherical to spherical to decreasing diameter spherical is shown in Fig. 1H to highlight the morphology changes from Figs. 1A–G.

To gain further insights into the influence of reagent concentrations and solution chemistry on final $MnCO_3$ precipitate particle morpholology, a series of experiments were conducted where the same sequence of increasing Mn^{2+} concentrations was used as described earlier (1.5–12 mM in 1.5 mM increments, as used in Fig. 1); however, the NH_4HCO_3:$MnSO_4$ ratio was varied as well with ratios of 10:1, 5:1, and 1:1 in addition to the 40:1 sequence described above. The detailed SEMs of the resulting particle morphologies can be found in the Supplemental Material in Figure S1 (10:1 reagent ratio), Figure S2 (5:1 reagent