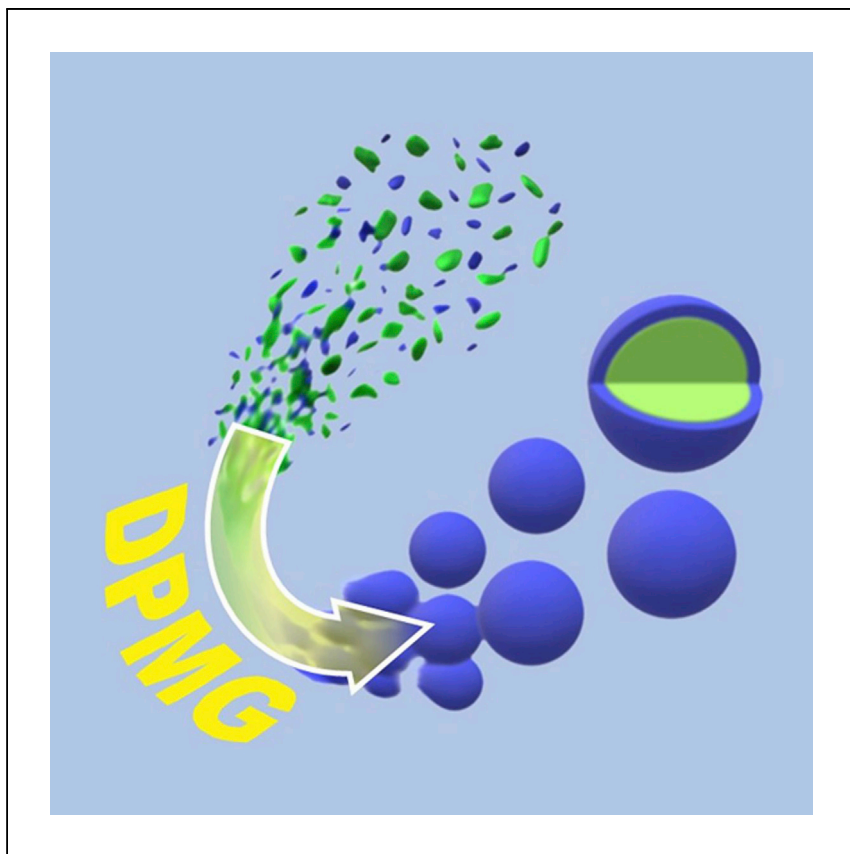


Report

Engineered Particle Synthesis by Dry Particle Microgranulation



Monodisperse $\sim 10\text{-}\mu\text{m}$ engineered particles are important for many applications, including the electrode materials for Li-ion batteries. Obrovac et al. introduce a new dry method of making engineered particles at the $\sim 10\text{-}\mu\text{m}$ scale with $\sim 100\%$ yields, allowing for the synthesis of spherical, tetrahedral, and even internally compositionally modulated particles.

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HIGHLIGHTS

A method of making monodisperse engineered $\sim 10\text{-}\mu\text{m}$ particles is introduced

Core-shell, spherical, and tetrahedral particles demonstrated at $\sim 100\%$ yield

Spherical layered oxides for Li-ion batteries made from metal oxide powders

Spherical onion-type graphite synthesized in bulk from fine natural graphite flakes

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Report

Engineered Particle Synthesis
by Dry Particle MicrogranulationM.N. Obrovac,^{1,2,3,4,*} Lituo Zheng,^{1,3} and M.D.L. Garayt¹

SUMMARY

Uniform $\sim 10\text{-}\mu\text{m}$ particles are important in several applications, including the metal oxide and graphite active materials in Li-ion batteries. Current production methods (e.g., co-precipitation and spheronization) can be wasteful and have limited composition scope. Here, we report dry particle microgranulation (DPMG) as a method for synthesizing highly engineered particles by consolidating fine, even submicron particles into particles that are tens of microns. DPMG enables the precise control of particle internal composition variation, shape, and morphology that is not possible by previous methods and at near 100% yields with no waste. Using this method, we show that Li-ion battery graphite and metal oxide particles, including those with designed internal composition variation, can be made at 100% yield with little waste. We believe that DPMG could be used in many fields to reduce the cost and environmental impact of particle synthesis and to enable the synthesis in bulk of new, highly engineered particles.

INTRODUCTION

Monodisperse fine particles on the order of $10\ \mu\text{m}$ are highly important for many applications, including power metallurgy,¹ liquid chromatography,² powder lubricants,³ catalyst supports,⁴ and Li-ion batteries.⁵ Often, such particles are required to have controlled internal structures and internal composition variation. Methods of producing fine particles of a uniform size and shape include grinding and classifying,⁶ spray-drying,⁶ gas atomization,⁷ precipitation,^{6,8} and spheronization,⁹ depending on the application. Wet methods are often used, with the liquid either being present as a reaction medium (e.g., precipitation) or reducing aggregation (e.g., wet grinding); however, such methods inevitably require filtering and/or drying steps, which can be energy and time intensive and may produce contaminated wastewater. Typically, most fine monodisperse particle syntheses include a classification step in which fine and coarse particles are removed. In many cases, particles outside the desired size range, especially fine particles, cannot be reprocessed and are lost as waste. Few processes exist in which internal particle composition can be controlled to make gradient or core-shell particles. Coprecipitation is an important method to accomplish this, but it is limited in that the precursors must be water soluble and the different precursors must precipitate at a similar pH.⁸

Li-ion batteries are a major application of fine highly engineered particles and will be used as a case example of advanced particle synthesis in this article. The best active materials in Li-ion batteries are uniform $\sim 10\text{--}20\ \mu\text{m}$ spheroidal particles of graphite (at the anode) or lithium transition metal oxides (at the cathode).⁵ Such particles have good packing properties and low surface area to reduce surface reactions with electrolytes that are associated with capacity fade. The majority of Li-ion battery

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cathode materials are lithium manganese nickel cobalt oxides (NMC) or lithium nickel cobalt aluminum oxides (NCA). These materials are made by a coprecipitation process, typically in a continuously stirred tank reactor (CSTR), shown schematically in Figure S1A. The CSTR produces a suspension of mixed metal carbonate particles in water from metal sulfate salts (in some instances, mixed metal hydroxides can also be made). The precise control of feedstock addition rate, temperature, stirring, pH, and chelating agents is necessary to achieve dense spherical metal carbonate particles. These conditions restrict the composition range of NMC that can be made. The CSTR process is also resource intensive. A typical production facility making 6,500 kg NMC per day can consume 99,000 L/day of water.¹⁰ The product carbonates can have a wide particle size distribution, requiring grinding and classifying, producing fine particles as another waste product (amount proprietary). Finally, the dried carbonate is combined with a lithium source and heated to produce battery-grade NMC. The final composition of the NMC or NCA made by this method is restricted to those elements that are compatible with the CSTR process. Because of the energy consumed, wastewater, chemical waste, and the many process steps involved, the CSTR process is expensive, with the raw material cost of NMC being estimated to account for only 50% of the total production cost.¹⁰ CSTR feedstock costs are also high. For instance, NMC production is leading to a shortage of nickel sulfate feedstock (referred to in the industry as a “class 1” Ni product). Much less expensive class 2 nickel products (including nickel oxide) are not compatible with the CSTR process. Enabling the use of class 2 nickel in NMC production could reduce costs substantially.

Both artificial and natural graphite powders are used as anode materials in Li-ion batteries.⁵ Artificial graphite spheres can be made directly by heating organic precursors, such as petroleum pitch, to $\sim 3,000^{\circ}\text{C}$. Increasingly, spheroidal (or potato-shaped) natural graphites are used in Li-ion batteries to reduce costs.¹¹ These are made by first grinding and classifying natural graphite to obtain a powder with the desired size distribution ($\sim 10\text{--}20\ \mu\text{m}$ diameter) and then spheronizing the sized powder. However, this process can be as low as 30% efficient (e.g., <http://www.northerngraphite.com/about-graphite/graphite-growth-markets/lithium-ion-batteries>), producing a large amount of fine particle ($<5\ \mu\text{m}$) waste. The spheronized powders are finally heated to $\sim 3,000^{\circ}\text{C}$ or chemically treated (typically with HF or HCl) as a purification step before use in Li-ion batteries. In the resulting spheronized particles, the graphite layers can be rolled up in the form of a clenched fist.¹² This morphology reduces the exposure of the edges of the reactive graphite basal planes with electrolytes; however, basal plane edges are still exposed at either end of the “fist,” requiring the particles to be carbon coated.

In this article, a dry granulation method is introduced to produce small ($<100\ \mu\text{m}$) particles. Granulation is an attractive, low-cost, high-yield method in which small particles may be aggregated into larger particles and is used in the production of fertilizers, pharmaceuticals, toners, pigments, fillers, and catalysts.^{13,14} However, both wet and dry methods of granulation have difficulty in making uniform particles $<100\ \mu\text{m}$ in diameter, and the resulting particles can often contain internal voids. Here, we demonstrate a new dry granulation method in which submicron particles can be granulated into monodisperse and dense $\sim 10\text{-}\mu\text{m}$ particles of specific shape and size at near 100% yields with no waste. We call this method “dry particle microgranulation” (DPMG). Here, Li-ion battery spherical graphite, metal oxide cathode, and engineered core-shell metal oxide cathode particles are synthesized by DPMG as specific examples of its usefulness. In some cases, the particles produced are unique (e.g., tetrahedral mixed oxide particles, onion-type graphite) and cannot

be made by any other method known to us. The simplicity, high yields, and flexibility of DPMG to make highly engineered and unique particles makes it highly attractive for particle synthesis.

RESULTS

Description of the DPMG Process

DPMG was discovered in the process of coating different particles by the mechanofusion method, which we have described in previous publications,^{15,16} and is shown in [Figures S1B](#) and [S1C](#). Briefly, in mechanofusion, particles are introduced into a spinning drum (~1,000–5,000 rpm). The spinning motion forces the particles onto the wall of the drum, where they must pass through a small gap between the rotating drum and a stationary press head. A stationary blade then scrapes the powder off the wall. Mechanofusion is commonly used as a spheronization method. It can also be used as a method to coat particles: a mixture of small and large particles processed by mechanofusion can result in the small particles being coated onto the surface of the larger particles.¹⁵

While in the process of coating small particles onto larger particles by mechanofusion, in our experiments, the small particles sometimes did not adhere to the large particles. In these cases, we noticed that the small particles tended to become granulated into spherical particles that had a smaller diameter than the larger particles and a very narrow particle size distribution. This seemed to us to be an attractive method of granulation, in which fine submicron feedstock particles (FPs) could be aggregated into micron-sized particles by the action of larger template particles (TPs) during mechanofusion. For the process to work, we reasoned that the TPs needed to be spherical, have an average size that was somewhat above our target product particle size, have a narrow particle distribution, be smooth (so as not to stick to the small FPs), and hard (so as not to deform or wear during the DPMG process). From these criteria, and having ~5–30 μm as target particle sizes, 50 μm ZrO₂ spheres were selected as TPs (shown in [Figure 1A](#)).

Synthesis of NMC Particles

To make NMC with the composition LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC111), the FPs were prepared by combining NiO, MnO, Co₃O₄, and Li₂CO₃ in stoichiometric proportion (but with 10% excess lithium) in a jar mill for 1 week. This produced amorphous FPs with submicron grains (scanning electron microscopy [SEM] image shown in [Figure 1B](#)). It is well known that laboratory jar mills (<0.3 m diameter) are far more inefficient than large mills (≥2 m diameter) and that processing time reduces as the mill diameter increases. Therefore, it is expected that any large-scale milling process would have substantially less processing time than our laboratory jar mill.¹⁷ The FPs were then combined with the TPs, processed by mechanofusion, and then separated from the TPs by sieving. The resulting particles are shown in [Figure 1C](#). They are rounded and have an average size of ~25 μm. The lack of fine particles is remarkable. They are comparable in size and distribution to commercial NMC particles (as shown in [Figure S2](#)). Even more remarkable is that the DPMG NMC particles have not been classified, while further improvements in particle distribution could be made if a classification process were used. Unlike CSTR, any waste from a classification process of DPMG particles could be ground and DPMG processed again. From these results, we believe that this process can operate at near 100% yield. Under different conditions, tetrahedrally shaped NMC particles can be made, as shown in [Figure 1D](#). We are studying the unique packing properties of these tetrahedrally shaped particles to see whether they can increase the cathode rate performance.

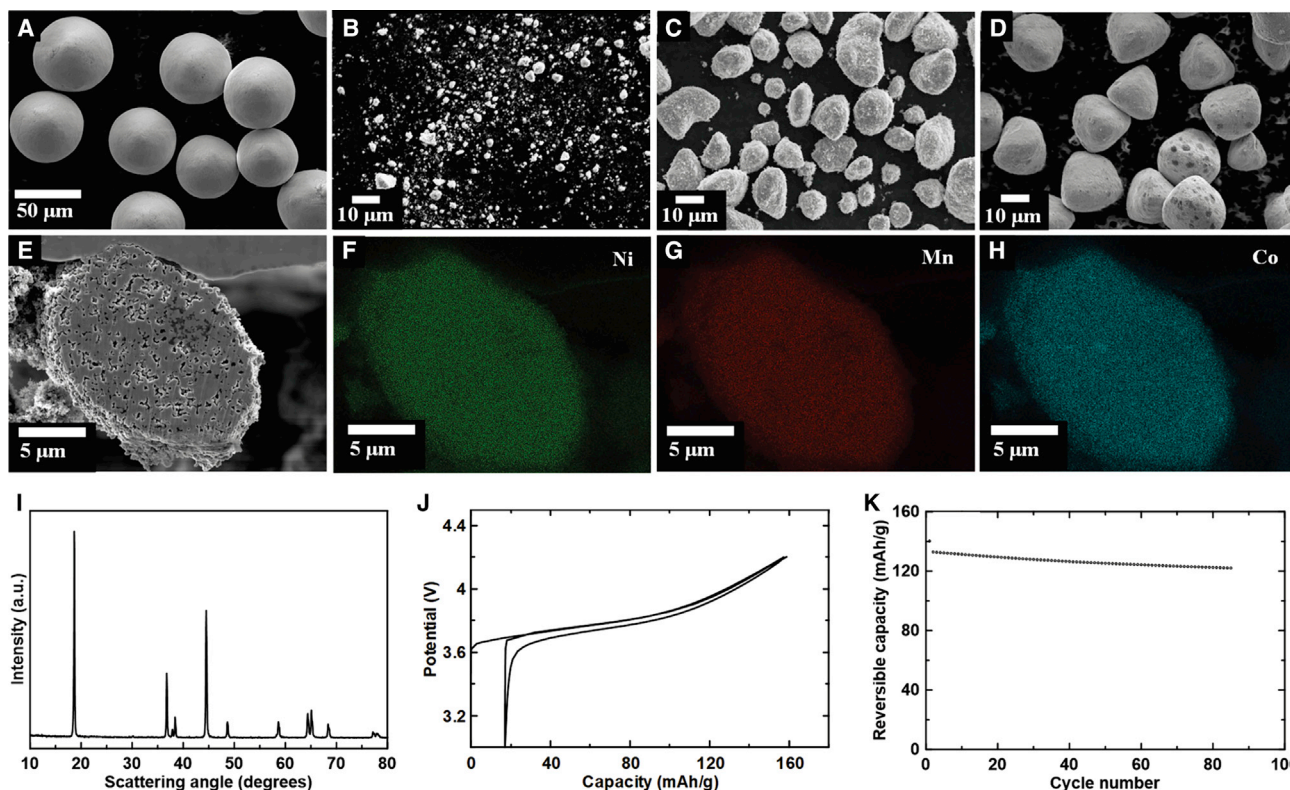


Figure 1. Synthesis of NMC Particles

(A–D) SEM images of (A) 50 μm ZrO_2 TPs, (B) NMC FPs as produced by jar milling, (C) DPMG processed NMC FPs, and (D) DPMG NMC 111. (E–H) Cross-section (E) and EDS mappings of DPMG NMC111 for Ni (F), Mn (G), and Co (H). (I–K) XRD pattern (I), potential profile (J), and cycling performance (K) of DPMG NMC111.

Cathode product particles were then heated to produce DPMG NMC111. Cross-sectional and energy-dispersive X-ray spectroscopy (EDS) SEM images are shown in Figures 1E–H. DPMG NMC111 particles contain a uniform element distribution and comprise $\sim 0.5\text{-}\mu\text{m}$ grains and some voids. We have eliminated these voids in other samples (e.g., Figure S3A); however, the presence of some voids is desirable for good lithiation kinetics. The X-ray powder diffraction (XRD) pattern of DPMG NMC111 is shown in Figure 1I. The material is phase pure and highly crystalline. The potential profile and cycling performance of DPMG NMC111 is shown in Figures 1J and 1K. In a Li-half cell, the performance of DPMG NMC111 is comparable to commercial NMC made from CSTR,^{18,19} even though the DPMG particles are unmodified by doping and have no special coatings. The surface morphology of the DPMG particles can be changed by varying the synthesis method. For instance, if jar-milled NiO, MnO, and Co_3O_4 precursor particles are DPMG processed and then combined with Li_2CO_3 during the sintering process, then the final particles resemble more closely those made conventionally by CSTR (see Figure S4). Much more work is needed to understand the influence of precursor chemistry, grain orientation, grain shape, internal porosity, and particle shape (all parameters that can be controlled by a combination of DPMG and sintering conditions) on the electrochemical performance of these materials.

Synthesis of Core-Shell NMC Particles

A careful examination of the cross-sectional SEM images of different DPMG NMC samples showed that the crystallites near the center of the product particles often

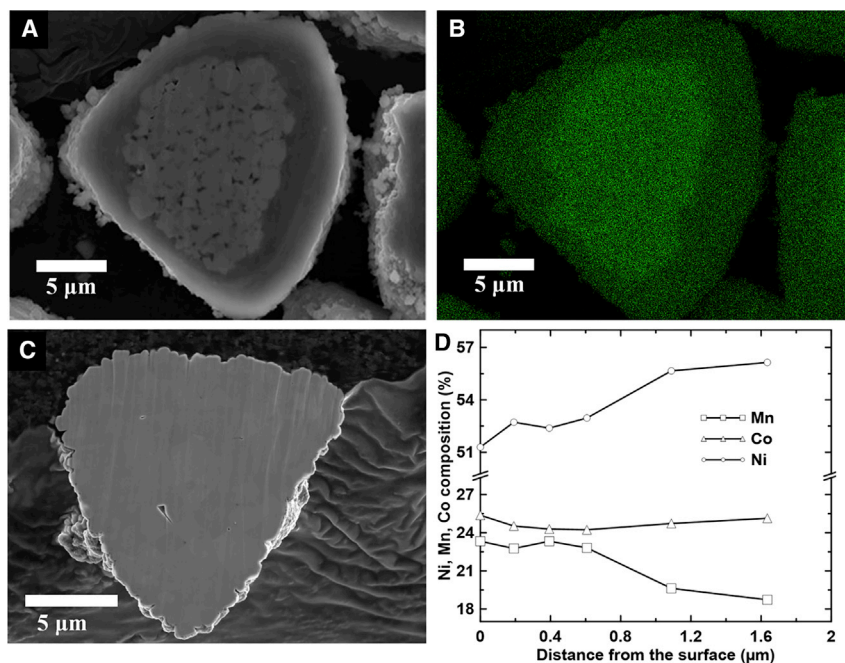


Figure 2. NMC Particles with a Ni-Rich Core and a Mn-Rich Shell

(A) Cross-sectional image of an NMC particle designed to have a Ni-rich shell and a Mn-rich core, before sintering.

(B) EDS Ni mapping of the same product particle as (A).

(C) Cross-sectional image of an NMC particle designed to have a Mn-rich shell and a Ni-rich core, after sintering.

(D) Ni, Mn, and Co composition as a function of the distance from the surface of the sintered NMC particle shown in (C).

have a larger size than crystallites closer to the surface of the product particles. This suggests that during DPMG processing, the precursor particles are segregated to be near the core or surface of the product particles according to their size. This feature enables precise variation of the internal composition of product particles by processing mixtures of precursor particles of different compositions and particle sizes. This is highly desirable in a number of applications, including Li-ion battery cathode material particles, which ideally constitute a phase near their core that can store a large amount of lithium, while having a phase near their surface that is stable with electrolytes at high potentials.

As a proof of concept, NMC particles with a Ni-rich core and a Mn-rich shell were synthesized by jar milling NiO, MnO, Co₃O₄, and Li₂CO₃ oxides to make a Ni-rich precursor with an NMC ratio of 622 and a Mn-rich precursor with an NMC ratio of 111. The Ni-rich precursor was then heated at 900°C to increase its grain size. The two types of precursors were then combined, and the mixture was processed by DPMG. This process is shown schematically in Figure S5. An SEM image and an EDS map of a cross-section of a typical product particle before sintering is shown in Figures 2A and 2B, respectively. An SEM image at lower magnification, showing the cross-sections of many particles is shown in Figure S6. As expected, the larger Ni-rich precursor particles and the smaller Mn-rich precursor particles are well segregated in the core and shell of the product particles, respectively. After sintering, a concentration-gradient particle forms due to the diffusion of transition metal ions during high-temperature heating (Figure 2C). However, a Ni-rich core and a

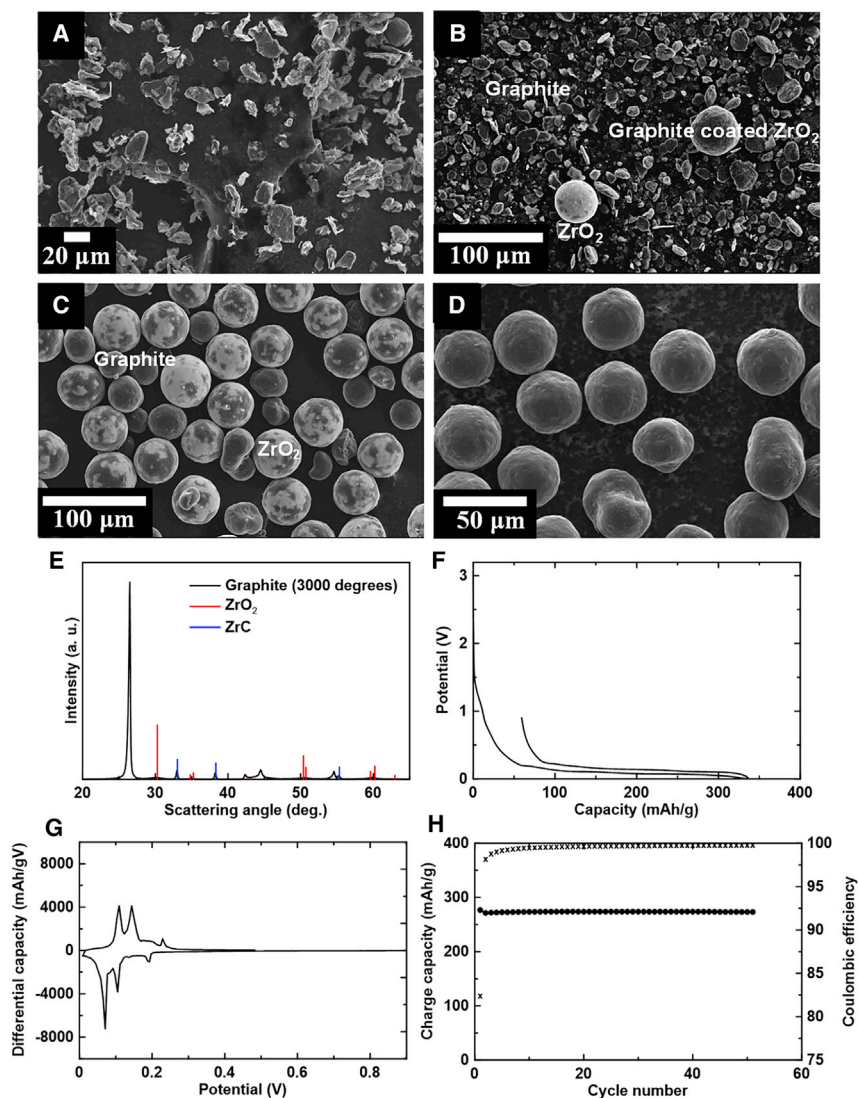


Figure 3. DPMG Processing Flake Natural Graphite

(A and B) SEM images of (A) natural graphite flakes, (B) natural graphite, and ZrO₂ TPs after being subjected to microgranulation process for 30 min.

(C) SEM images of natural graphite flakes and ZrO₂ TPs after being subjected to the microgranulation process for 12 h.

(D) SEM image of spherical natural graphite separated from the ZrO₂ TPs.

(E–H) XRD pattern (E), potential profile (F), differential capacity profile (G), and cycling performance (H) of DPMG graphite.

Mn-rich shell were still maintained, as shown in Figure 2D. More details of the synthesis, structure, and electrochemistry of core-shell particles made using the DPMG method will be reported in future publications.

Synthesis of Spherical Natural Graphite

We have found that DPMG is also an excellent method for synthesizing spherical graphite with little or no waste. Figure 3 shows the result of DPMG processing flake natural graphite (Figure 3A). In the initial stage, the graphite begins to coat the surface of the TPs. After further processing, the graphite coating becomes thicker

(Figure 3B) and then spalls off, forming graphite spheres (Figure 3C). This process is shown schematically in Figure S7. The spheres are highly turbostratic, requiring subsequent heating to convert them to crystalline graphite. Initially, we separated the graphite from the TPs by density using diiodomethane; the separated spheres are shown in Figure 3D. This resulted in internal porosity and some spheres exploding during graphitization, presumably due to intercalation of the diiodomethane into the graphite. If separated using a sieve, this porosity can be avoided, and all of the spheres remain intact during heating (Figure S3B). Nevertheless, the porosity introduced by diiodomethane shows that the resulting graphites have an onion-type structure, with the graphite layers oriented in nested concentric spheres, as shown in Figure S8. This type of graphite is desirable for lubrication applications. It is also desirable for battery applications, since the reactive edges of the graphite basal planes are not exposed to the electrolyte. However, despite considerable efforts, onion-type graphites have previously only been made in small amounts and with nano-dimensions.

The graphitized spherical graphites made here by the DPMG process are highly crystalline, as shown in Figure 3E, with a small amount of ZrO₂ and ZrC impurity from the TPs. Their particle distribution is narrow and their surface area is low (0.9 m²/g), which is desirable for battery applications. The potential profile and differential capacity of DPMG graphite (Figures 3F and 3G) demonstrates good staging plateaus, and good cycling was achieved (Figure 3H), albeit at a lower capacity compared to commercial graphite due to the TP impurity. Further optimization and characterization studies of DPMG graphites are needed to fully explore their electrochemistry, especially the amounts of impurities introduced by the DPMG method. Another batch of DPMG graphite with no TP impurity has yet to be fully graphitized and further results will be described in a future publication.

DISCUSSION

These results suggest that DPMG could be highly useful for fine-particle synthesis. In the case of cathode battery production, the advantages of DPMG over solution-based production methods are apparent from Figure S1A. The DPMG process has almost one-third of the process steps as CSTR, produces no waste, and has near 100% yield. In addition, its feedstocks are much more flexible, potentially enabling significant cost savings in processing and raw materials costs. Furthermore, improved NMCs with compositions incompatible with CSTR and designed with precise internal composition variations could be made by DPMG. The advantages for spheroidal graphite production are also clear. By recovering and reusing the TP particles, the process produces no waste and near 100% yield. This presents a huge raw materials savings compared to conventional spheronization. Furthermore, we believe that the onion-type graphite produced by DPMG is potentially superior to conventionally spheronized graphites in battery applications.

This article represents only our initial findings with this new process. We are investigating process optimization for implementing DPMG on a commercial scale, especially in lowering the processing time, increasing the FP:TP ratio, and determining the impact of larger-scale equipment on processing efficiency. We are also investigating other uses for DPMG, as we expect it could have applications in many fields.

In summary, we have discovered a new low-cost and environmentally friendly route for producing complex powder particles with no waste and 100% yields. We believe that this will lead to significant cost savings in engineered powder particles and

enable the synthesis of new materials tailor-made with precise control of particle size, shape, and internal composition variation. The flexibility of the method represents a large area of exploration of advanced particle synthesis for application in many fields.

EXPERIMENTAL PROCEDURES

Resource Availability

Lead Contact

Information and requests for resources and materials should be directed to the Lead Contact, Mark Obrovac (mnobrovac@dal.ca).

Materials Availability

Materials synthesized in this manuscript can be obtained by request to the Lead Contact.

Data and Code Availability

The published article includes all datasets generated or analyzed during this study.

NMC Cathode Synthesis

NMC cathode FPs were made by milling in air 60 g stoichiometric amounts of NiO (99%, Sigma-Aldrich), MnO (99%, Sigma-Aldrich), Co₃O₄ (99.7%, Alfa Aesar), and Li₂CO₃ (99%, Alfa Aesar) with 10% excess Li₂CO₃ with 10 kg of 0.5-in stainless steel balls in a 5-L stainless steel jar mill (0.2 m diameter, US Stoneware) for 1 week at 85 rpm. A total of 225 g ZrO₂ TPs (Glen Mills) and 15 g NMC FPs (~50 mL total powder volume) were placed in a mechanofusion machine (ANG mill AM-15, Hosokawa Micron) and processed for 21 h at 1,000 rpm with a 1.4-mm press-head gap and a 0.5-mm scraper gap. The product was then separated from ZrO₂ particles with a 38- μ m sieve and heated at 900°C for 12 h in air.

Spherical Graphite Synthesis

A total of 225 g ZrO₂ TPs and 25 g natural graphite FPs (230U, Asbury Graphite Mills) (~50 mL total powder volume) were processed by mechanofusion at 1,500 rpm for 12 h. The product was then either separated from ZrO₂ particles by sieving or by using diiodomethane (99%, ReagentPlus, Sigma-Aldrich) and then heated at 3,000°C for 3 h in Ar.

Materials Characterization

Sample morphology and elemental distribution were measured using field emission scanning electron microscopy (FESEM, TESCAN MIRA 3) equipped with an EDS or an SEM (JEOL JSM-840). Cross-sections of samples were prepared using a cross-section polisher (JEOL, IB-19530CP). XRD patterns were measured using a Rigaku Ultima IV X-ray diffractometer with Cu K α radiation.

Electrochemical Characterization

Electrodes were prepared from slurries containing active materials, binder (polyvinylidene fluoride, Kynar HSV 900), and carbon black (Super C65, Imerys Graphite and Carbon) in a ratio of 92:4:4 for NMC and 90:5:5 for graphite, and an appropriate amount of *N*-methyl-2-pyrrolidone (anhydrous 99.5%, Sigma-Aldrich). Slurries were mixed using a planetary mixer (KK-250S Mazerustar, Kurabo Electronics), coated onto aluminum foil (NMC) or copper foil (graphite) using a 0.15-mm coating bar, and dried at 120°C in air. Circular electrode disks were punched from the coating and dried under vacuum at 120°C overnight before cell assembly. Coin cell batteries (2325 size) were assembled with 1 M LiPF₆ in a solution of ethylene

carbonate, diethyl-carbonate, and monofluoroethylene carbonate (3:6:1 v/v/v, all from BASF) as an electrolyte solution, with 2 layers of microporous separator (Celgard 2300), 1 layer of polypropylene blown microfiber separator (BMF, 3M Company), and lithium foil as the counter-reference electrode. Cells were cycled at $30.0^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ with a Maccor Series 4000 Automated Test System.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.xcrp.2020.100063>.

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AUTHOR CONTRIBUTIONS

M.N.O. conceived the idea for the study. M.N.O. and L.Z. designed the experiments. L.Z. and M.D.L.G. performed the experiments. M.N.O. and L.Z. wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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