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Custom Ultrasonic Spray Pyrolysis Equipment for the Scalable Synthesis of $LiFePO_4$ Cathode Materials

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ABSTRACT

Lithium iron phosphate is a promising cathode material for lithium-ion batteries owing to its safety, long cycle life, and environmental compatibility, but its performance strongly depends on the synthesis route. In this work, we report a custom-designed ultrasonic spray pyrolysis system equipped with a six-zone programmable furnace and a heated electrostatic precipitator for scalable and controlled LFP/C synthesis. Compared with conventional single-zone USP setups, this apparatus enables staged droplet-to-particle transformations, suppressing hollow morphologies and improving precursor uniformity. LFP/C powders synthesized in the 400-600 °C range exhibited poorly crystalline or partially amorphous structures as-sprayed, which transformed into phase-pure olivine $LiFePO_4$ after annealing at 600 °C for 3 h under Ar. SEM revealed that spherical, submicron precursor particles (~200 nm - 1 μm) with smooth surfaces were produced directly by USP, while post-annealing preserved the morphology but introduced coarser textures and surface porosity. Such microstructural evolution is expected to balance tap density and Li^+ transport pathways, consistent with prior studies of USP-derived LFP/C. Comparative analysis with two-phase nozzle and flame spray pyrolysis systems shows that the combination of gradient thermal control and electrostatic deposition in our setup improves the quality of the resulting powders and provides a promising combination of laboratory precision and potential scalability. These results demonstrate that the custom USP approach is an efficient and flexible platform for producing high-quality LFP/C cathode powders with controllable morphology and crystallinity.

1. Introduction

Lithium iron phosphate ($LiFePO_4$, LFP) is one of the most extensively studied cathode materials for lithium-ion batteries because of its intrinsic safety, long cycle life, environmental compatibility, and competitive cost [1-3]. Its electrochemical performance, however, is highly dependent on the synthesis route, which determines the phase purity, particle morphology, and size distribution [4, 5].

Numerous synthesis routes have been reported for obtaining LFP, including solid-state reaction [6], sol-gel processing [7], hydrothermal methods [8], and sol-gel-assisted hydrothermal techniques [9]. Each route, however, presents notable limitations: solid-state reactions demand extended high-temperature treatment; sol-gel methods involve multiple steps, long reaction times, and inefficient solvent removal; and hydrothermal synthesis requires excess lithium precursors and several days of processing. Therefore, identifying a more efficient synthesis strategy for LFP with enhanced electrochemical performance remains a critical challenge. In this context, ultrasonic spray pyrolysis (USP) has emerged as a promising alternative, offering continuous, scalable production of fine, homogeneous particles with controllable morphology [10].

Spray pyrolysis is a versatile route for synthesizing LFP and related electrode materials, yet reported systems vary widely in their atomization principles,

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reactor configuration, and collection efficiency. Conventional laboratory setups often employ single- or two-zone tubular furnaces, where the droplet drying, salt decomposition, and crystallization processes occur in rapid succession with limited control. For example, Yang et al. [11] demonstrated that USP at 450-650 °C followed by annealing yields carbon-coated LFP microspheres, though precise control of morphology required post-treatment. Konarova and Taniguchi [12] similarly showed that as-prepared LFP powders from USP were spherical but partially covered with Fe_2O_3 surface layers, requiring sintering at 600-800 °C to obtain phase-pure LFP/C with acceptable electrochemical capacity. In contrast, flame spray pyrolysis systems emphasize high-temperature, turbulent combustion, as in Hamid et al. [13], who produced nanosized $FePO_4$ precursors with surface areas up to 218 $m^2{\cdot}g^{-1}$, later converted to LFP/C composites with >145 $mA{\cdot}h{\cdot}g^{-1}$ capacity. Halim et al. [14] further demonstrated that flame spray pyrolysis yields spherical but polydisperse LFP particles, where crystallinity strongly depended on flame temperature and post-annealing. Other groups explored two-fluid nozzle atomization, enabling suspension-based carbon sources but with broader particle size distributions and limited phase crystallization without high-temperature calcination. More recently, hybrid processes such as ultrasonic-assisted ball milling plus carbothermal reduction and spray drying with negative ion generators have been introduced to tailor particle size and mitigate defects like Li-Fe antisite disorder.

In this context, our custom-built USP apparatus offers several advantages over previously reported systems. The six-zone horizontal furnace (100-800 °C, independently programmable) allows staged heating, enabling sequential drying, decomposition, and crystallization of droplets, in contrast to the single thermal environment of most tubular furnaces. This gradient control reduces hollow particle formation and enhances crystallinity without excessive sintering. Furthermore, instead of conventional cyclone or bag-filter collection, our system integrates a heated electrostatic precipitator, which efficiently captures fine submicron powders while minimizing agglomeration. Combined with the use of an ultrasonic nebulizer operating at 1.7 MHz, which produces narrow droplet size distributions similar to the systems of Yang et al. [11] and Konarova [12], the apparatus ensures one-droplet-one-particle transformation with high yield and reproducibility. Overall, compared with flame-based systems or simpler USP units, the multizone gradient design and electrostatic collection distinguish this USP setup as a hybrid between lab-scale precision and semi-pilot scalability, offering fine control over LFP particle morphology and phase purity.

2. Experimental part

2.1. Materials

The precursor solution was prepared by dissolving 1.38 g lithium nitrate powder ($LiNO_3$, 99% extra pure, Thermo Scientific), 8.08 g iron nitrate nonahydrate crystals ($Fe(NO_3)_3{\times}9H_2O$, Sigma-Aldrich) and phosphoric acid 1.96 g (H_3PO_4, 85% ACS reagent, Sigma-Aldrich) a stoichiometric ratio into 100 mL of distilled water. The concentration of Li^+, Fe^{3+} and PO_4^{3-} were all 0.2 mol/L. As a source of carbon 0.68 g sucrose ($C_{12}H_{22}O_{11}$, ≥ 99.5%, Sigma-Aldrich) in concentration 0.02 mol/L was added to form a $LiFePO_4$/C.

2.2. Ultrasonic spray pyrolysis synthesis of LFP/C

Fig. 1 demonstrates a scheme of the USP unit (made by special order by BesSaiman Group, Almaty, Kazakhstan). The unit system consist of a droplet generator – nebulizer, a flow rate controller, peristaltic pump, furnace with a divided temperature sections to 6 zone, and each of zone could be settled separately to create a temperature gradient, which was varied from 400 to 600 °C.

The spray pyrolysis setup consisted of an ultrasonic nebulizer (3) supplied with precursor solution (1) through a peristaltic pump (2) and integrated into a heating circulation system (5). The generated aerosol was carried into a laminar-flow reactor, consisting of a quartz tube (7) with diameter of the tube 5 cm and a length of 1.5 m, placed inside a horizontal tubular furnace (8). At the outlet, the powders were collected in a quartz electrostatic precipitator (11) equipped with tungsten wire electrodes, a grounded plate, a quartz collection plate, and a chamber heater. A DC high-voltage source was applied to the tungsten wires to facilitate particle capture.

The precursor solution was atomized at 1.7 MHz by the ultrasonic nebulizer, producing droplets that were transported into the reactor by Ar gas flowing at 2 $L{\cdot}min^{-1}$. Inside the furnace, maintained between 400-600 °C, the droplets underwent solvent evaporation, solute precipitation, drying, decomposition, and annealing, ultimately forming solid particles. A typical gradient was set as follows: zone 1 – 400 °C, zone 2 – 450 °C, zone 3 – 500 °C,

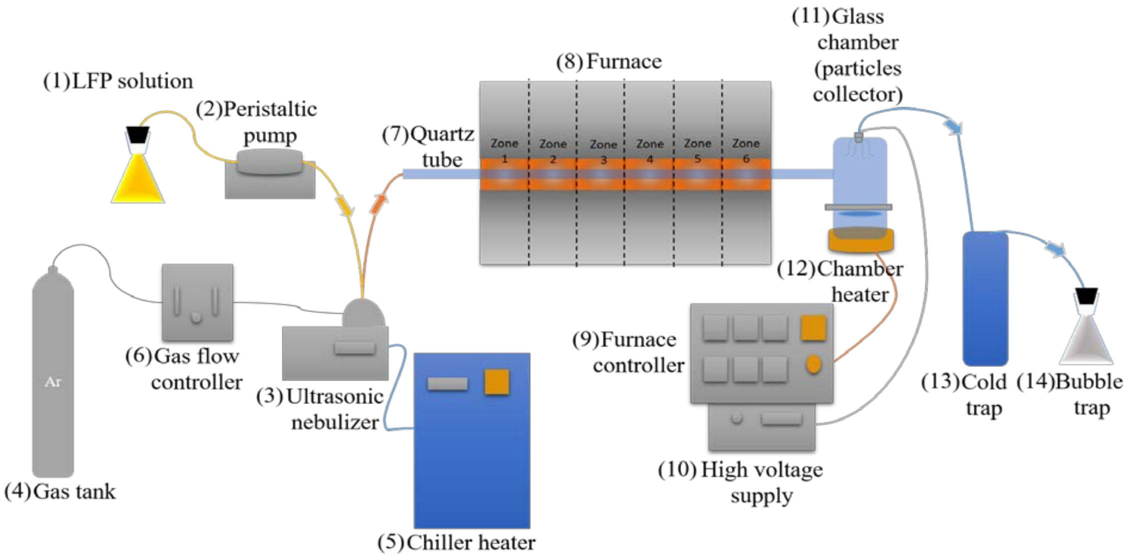

Fig. 1. Principle scheme of custom USP equipment.

zone 4 – 550 °C, zone 5 – 600 °C, zone 6 – 600 °C. The collected powders were deposited on the heated quartz plate, which was maintained at 150 °C, while the exhaust gases were purified by passing through a cold trap (13) and a bubble trap (14).

For the preparation of LFP/C, the samples prepared at USP unit in the range of gradient temperatures from 400 to 600 °C, where each temperature zone was 25 cm in length. The temperature in each zone was independently controlled to establish a precise gradient profile. The total residence time of the aerosol droplets within the hot zone was approximately 3 s, calculated based on the carrier gas flow rate and quartz tube dimensions. The collected powders were then further annealed at temperatures from 500 to 700 °C for 3 h in a separate horizontal tube furnace under flowing Ar atmosphere (200 mL·min^{-1}).

The USP equipment used in this study was custom-built and is shown in Fig. 2. The unit consists of approximately 1.53-1.87 MHz ultrasonic nebulizer supplied by a peristaltic pump, a quartz-tube reactor (1.5 m length, 50 mm diameter) placed in a six-zone horizontal furnace (each independently programmable between 100 and 800 °C), and a heated electrostatic precipitator for fine-particle collection. Unlike conventional spray pyrolysis systems, which typically rely on single-zone furnaces and cyclone or bag-filter collectors, this design allows staged thermal processing and efficient capture of submicron powders. The multi-zone furnace provides precise gradient heating for sequential droplet drying, salt decomposition, and crystallization, while the electrostatic precipitator minimizes particle loss and agglomeration (see Fig. 2).

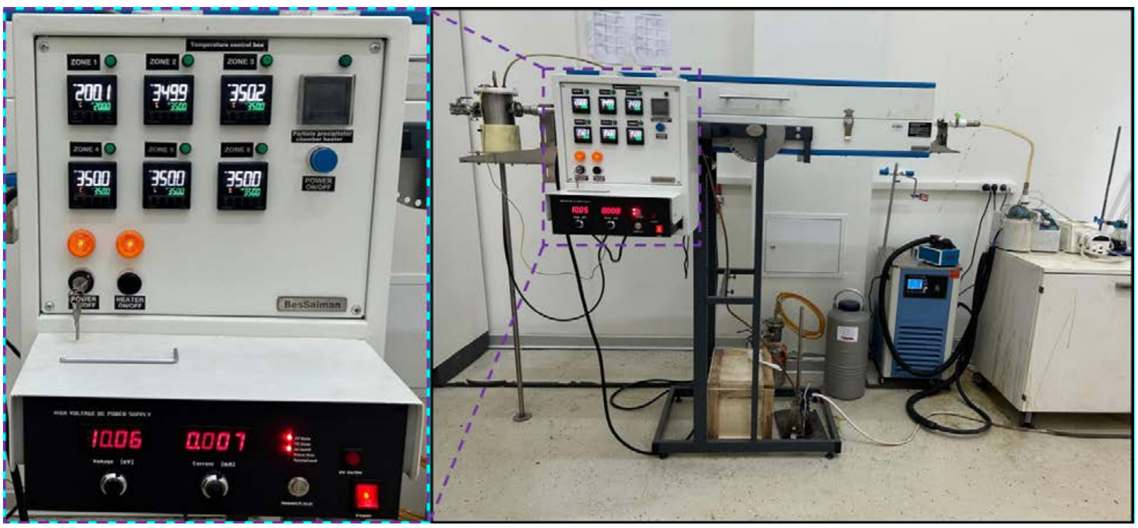

Fig. 2. Photograph of custom USP equipment.

2.3. Sample characterization

The crystalline phases were studied by X-ray diffraction (XRD, Rigaku, Mini-flex) analysis equipped with Cu-Kα radiation with a scan speed of 4° min^{-1} ranging from 10° to 70°. The surface morphology of the samples was examined by scanning electron microscopy (SEM, ZEISS Crossbeam 540) at 8 kV.

3. Results and discussions

3.1. XRD analysis

The phase composition and crystallinity of the LFP/C powders synthesized by USP were analyzed by XRD (Fig. 3). The as-prepared powders (black line) exhibit broad diffraction features with weak peak intensities, indicating that the product obtained directly from the USP equipment is predominantly poorly crystallized or partially amorphous. This result is typical of spray pyrolysis-derived powders, where rapid solvent evaporation and precursor decomposition limit crystal growth [11].

After post-annealing in an Ar atmosphere at 600 °C for 3 h (red line), the XRD pattern displays a series of sharp diffraction peaks that can be indexed to the orthorhombic olivine-type LFP phase (space group Pnma, JCPDS No. 81-1173). The prominent reflections at 2θ ≈ 17.0°, 25.6°, 29.8°, 35.5°, and 40.0° correspond to the (101), (111), (211), (311), and (401) planes, respectively, confirming the successful crystallization of phase-pure LFP [12]. No additional peaks corresponding to secondary phases such as Fe_2O_3, $FePO_4$, or Li_3PO_4 are detected, suggesting that the USP process combined with annealing yielded high-purity LFP powders.

The absence of carbon-related diffraction signals is attributed to the amorphous nature of the carbon coating, which is generally undetectable by XRD but is known to improve electronic conductivity [15]. The sharpening and intensification of diffraction peaks after annealing reflect significant enhancement of crystallinity and grain growth, which are essential for achieving efficient Li^+ diffusion in olivine LFP [14]. Similar findings have been reported for USP-synthesized LFP, where as-sprayed powders require post-annealing to achieve phase purity and electrochemical activity [11].

3.2. SEM analysis

The morphology of the LFP/C powders synthesized by USP was examined by SEM, and the representative micrographs are shown in Fig. 4. Prior to sintering (Fig. 4 a, b), the powders consist of loose agglomerates of nearly spherical particles with a relatively narrow size distribution. The particle diameters fall predominantly in the submicron range (~200 nm to 1 μm). High-magnification images reveal that the spheres possess smooth and dense surfaces, without noticeable porosity or fractures, confirming that the USP process promoted a one-droplet-to-one-particle transformation, yielding highly uniform LFP microspheres. These observations are consistent with earlier studies, which also demonstrated that USP provides nanostructured, spherical, and non-agglomerated LFP particles, in contrast to the irregular morphologies obtained by solid-state routes [11, 16, 17].

After sintering (Fig. 4 c, d), the spherical morphology is largely preserved; however, the particles display coarser surfaces and the

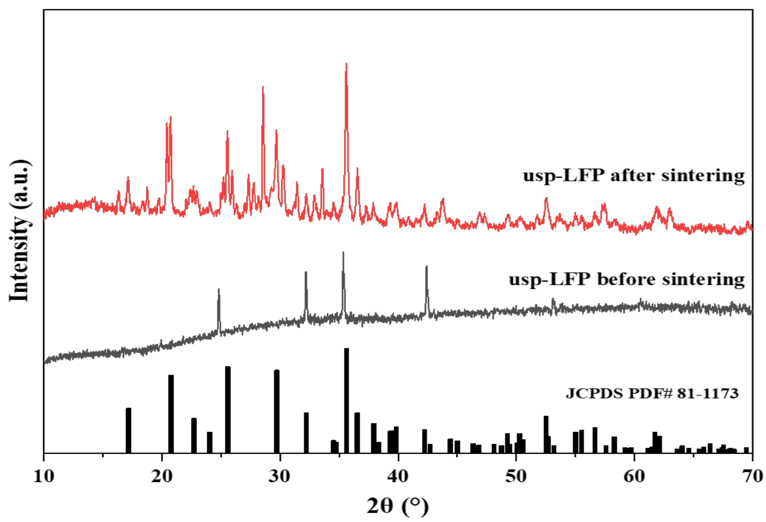

Fig. 3. XRD results of LFP/C samples before and after sintering.

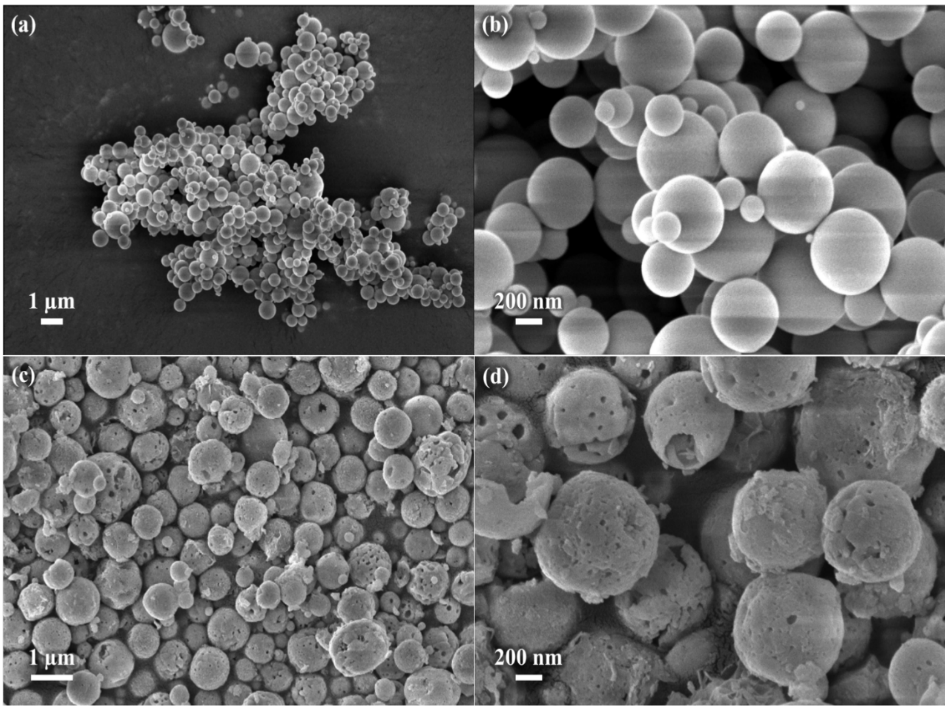

Fig. 4. SEM images of LFP/C nanoparticles (a, b) before and (c, d) after sintering.

development of pores and cavities across their structure. This morphological evolution is attributed to gas release and structural reorganization during thermal treatment. Similar findings have been reported for USP-derived LFP powders, where post-annealing enhances crystallinity but often results in particle densification accompanied by surface roughening or pore formation [12, 18].

Such morphological evolution has direct implications for electrochemical behavior. While the initial dense spherical structure contributes positively to tap density and short Li^+ diffusion pathways, the formation of surface pores after sintering may increase the electrode/electrolyte contact area, facilitating faster Li^+ transport but at the expense of volumetric energy density. Previous reports emphasize that the electrochemical performance of USP-derived LFP/C composites strongly depends on the balance between densification and controlled porosity introduced during heat treatment [19].

3.3. Comparative features of spray pyrolysis systems for LFP/C

As summarized in Table 1, our custom-built USP system differs significantly from conventional spray pyrolysis configurations reported in the literature. Early USP setups such as those of Yang et al. [11] and Konarova and Taniguchi [12] typically employed single-zone tubular furnaces operating at 400-650 °C, where the drying, decomposition, and crystallization steps occurred simultaneously. While these systems produced spherical LFP particles, the as-sprayed powders were often amorphous or surface-contaminated (e.g., Fe_2O_3 layers), and post-annealing was essential to obtain phase-pure olivine LFP. In our work, LFP powders were also synthesized in the 400-600 °C range and subsequently annealed to enhance crystallinity and phase purity. However, the key distinction of our setup is the six-zone furnace (100-800 °C), which enables precise staging of thermal transformations during droplet-to-particle conversion. This gradient control leads to denser and more uniform precursor particles prior to annealing, reducing the likelihood of hollow or fractured morphologies and ensuring greater reproducibility in particle size and shape compared with single-zone systems.

Two-fluid nozzle spray pyrolysis reactors, such as those described by Nakamura et al. [20], are more flexible toward suspensions and insoluble carbon sources but often yield broader particle size distributions and require higher calcination temperatures (≥750 °C) to crystallize the olivine phase. Flame spray pyrolysis systems, demonstrated by Hamid et al. [13] and Halim et al. [14], are advantageous for scalability and production of nanosized, high-surface-area $FePO_4$, yet they rely on turbulent flame environments, have limited morphology control, and generally require subsequent solid-state reactions with lithium salts to form LFP.

Table 1. Comparative features of spray pyrolysis systems for LFP/C

Feature	Conventional USP, [11, 12]	Two-fluid nozzle SP, [20]	Flame spray pyrolysis, [13, 14]	Our USP system (this work)
Atomizer type	Ultrasonic nebulizer (1.7 MHz), simpler dosing	Two-fluid nozzle (gas-liquid jet), suitable for suspensions	High-velocity air-blast atomizer into turbulent flame	Ultrasonic nebulizer (1.7 MHz) with peristaltic pump
Reactor design	Typically single-zone tube furnace (400-650 °C)	Dual alumina tubes, sequential heating zones (300 °C drying, 500 °C pyrolysis)	Open flame reactor, turbulent combustion zone	Quartz tube, 1.5 m length, 50 mm diameter
Furnace control	Single or dual heating zones, limited gradient	Two heating sections, fixed temps (300 and 500 °C)	Flame temperature >1000°C, uncontrolled gradients	Six independent zones, 100-800 °C, gradient heating
Collection method	Cyclone or simple bag filter	Bag filter	Downstream filter plates	Heated electrostatic precipitator with tungsten electrodes
Particle morphology	Spherical, but often require post-annealing; Fe_2O_3 surface impurities possible	Spherical to irregular; incorporation of carbon powders, but broad size distribution	Nano-sized $FePO_4$ or LFP; highly porous; needs post-processing	Spherical, submicron (200 nm-1 μm), dense or porous depending on gradient; reduced hollow particles
Crystallinity	As-sprayed amorphous, crystallization requires annealing at ~650 °C	As-sprayed low crystallinity; calcination at 750 °C needed for olivine LFP	As-prepared $FePO_4$ amorphous; requires solid-state post-reaction with Li_2CO_3	Poorly crystalline as-sprayed; phase-pure LFP after annealing at 600 °C
Carbon incorporation	Organic additives (e.g. sucrose), carbon coating; uneven distribution	Direct addition of AB or CNT powders; difficult to integrate uniformly	Glucose or organics during solid-state step: carbon matrix	Organic precursors: amorphous carbon coating; uniform after annealing
Advantages	Simple, low-cost, proven for lab-scale studies	Can handle suspensions with insoluble carbon sources	Scalable, industrially relevant, produces nanosized high surface area powders	Precise droplet-to-particle transformation; gradient control; high fine-powder recovery; morphology tunability
Limitations	Limited morphology control; prone to hollow spheres	Larger, less uniform particles; difficult crystallization	High energy input; requires post-solid-state reaction	More complex hardware; requires optimization of zone temps/flow
Overall efficiency	Moderate (requires post-treatment, losses during collection)	Moderate (carbon control improved, collection less efficient)	Moderate-low (scalable, but poor collection and reproducibility)	High (fine-particle yield, reproducibility, controllable morphology)

A further distinction of our system is the use of a heated electrostatic precipitator for powder collection. While conventional USP and two-fluid nozzle systems rely on cyclones or bag filters, our design enables efficient capture of submicron powders while suppressing condensate-induced agglomeration. Combined with ultrasonic atomization at 1.7 MHz, which provides a narrow droplet distribution and near one-droplet–one-particle transformation, this design ensures high precursor quality and minimizes powder loss. In addition, as the aerosol passes sequentially through the six independently controlled furnace zones, the flow experiences a staged thermal profile: initial solvent evaporation and droplet shrinkage occur in the lower-temperature zones, followed by salt decomposition and organic burnout in the mid-range zones, and finally crystallization and particle densification in the higher-temperature zones. This gradual thermal evolution reduces local turbulence, suppresses hollow particle formation, and ensures more uniform solidification compared with single-zone systems. Taken together, the integration of multizone gradient heating, electrostatic collection, and controlled annealing distinguishes our USP setup as a hybrid between laboratory-scale precision and semi-pilot-scale flexibility, offering both improved morphology control in the as-sprayed state and enhanced reproducibility of the final annealed LFP/C powders compared to conventional spray pyrolysis systems.

4. Conclusion

A custom-built USP system was successfully developed and applied to the synthesis of LFP/C powders. The apparatus integrates a six-zone programmable furnace (100-800 °C) with a heated electrostatic precipitator, enabling precise thermal staging and efficient submicron particle collection. Structural analysis confirmed that while as-sprayed powders synthesized at 400-600 °C were poorly crystalline, post-annealing at 600 °C produced phase-pure olivine LFP. SEM observations revealed uniform spherical particles before sintering, with surface porosity and coarsening introduced after annealing. These findings indicate that staged gradient heating enhances precursor uniformity and reduces defect-prone morphologies compared with conventional single-zone USP systems. Furthermore, comparative evaluation against two-fluid nozzle and flame spray pyrolysis setups demonstrates that the present USP system combines the fine control of laboratory-scale equipment with the potential scalability of pilot systems. Overall, this work establishes custom USP as a versatile and efficient route for tailoring LFP/C powders with improved reproducibility, controlled morphology, and potential for high-performance cathode applications.

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Специализированная установка ультразвукового спрей-пиролиза для масштабируемого синтеза катодных материалов $LiFePO_4$

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АННОТАЦИЯ

Литий-железо-фосфат ($LiFePO_4$) является перспективным катодным материалом для литий-ионных аккумуляторов благодаря своей безопасности, длительному сроку службы и экологической совместимости, однако его эксплуатационные характеристики в значительной степени зависят от метода синтеза. В данной статье представлена специально разработанная установка ультразвукового спрей-пиролиза, оснащенная шестизонной программируемой печью и подогреваемым электростатическим осадителем, предназначенная для масштабируемого и контролируемого синтеза $LiFePO_4$/C. В отличие от традиционных установок УСП с однозонными печами, данное оборудование обеспечивает поэтапное преобразование «капля-частица», подавляет образование полых морфологий и повышает однородность прекурсоров. Полученные в диапазоне 400-600 °C порошки $LiFePO_4$/C обладали слабо кристаллической или частично аморфной структурой в исходном (as-sprayed) состоянии, которая преобразовывалась в фазочистый оливиновый $LiFePO_4$ после отжига при 600 °C в течение 3 ч в атмосфере аргона. По данным СЭМ установлено, что непосредственно методом УСП формируются сферические субмикронные прекурсорные частицы (~200 нм-1 мкм) с гладкой поверхностью, тогда как после отжига морфология сохраняется, но появляются более грубые текстуры и пористость поверхности. Такая микроструктурная эволюция обеспечивает баланс между насыпной плотностью и путями транспорта Li^+, что соответствует данным предыдущих исследований УСП-производных $LiFePO_4$/C. Сравнительный анализ с системами на основе двухфазного сопла и пламенного спрей-пиролиза показывает, что сочетание градиентного термического контроля и электростатического осаждения в нашей установке способствует повышению качества получаемых порошков и обеспечивает перспективное сочетание лабораторной точности и потенциальной масштабируемости. Полученные результаты демонстрируют, что разработанный подход УСП является эффективной и гибкой платформой для получения высококачественных катодных порошков $LiFePO_4$/C с контролируемой морфологией и кристалличностью.

Ключевые слова: железофосфат лития ($LiFePO_4$), катодные материалы, ультразвуковой спрей-пиролиз, шестизонная печь, контроль морфологии, литий-ионные аккумуляторы.

$LiFePO_4$ катодты материалдарын ауқымды синтездеуге арналған арнайы ультрадыбыстық спрей-пиролиз қондырғысы

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АҢДАТПА

Литий темір фосфаты ($LiFePO_4$) литий-ионды аккумуляторлар үшін болашағы зор катодты материал болып табылады, себебі ол қауіпсіз, ұзақ циклді қызмет етеді және экологиялық тұрғыдан үйлесімді. Дегенмен, оның жұмыс сипаттамалары синтез әдісіне тікелей тәуелді. Бұл жұмыста біз алты аймақты (100-800 °C) жеке басқарылатын пешпен және қыздырылатын электростатикалық тұндырғышпен жабдықталған арнайы жобаланған ультрадыбыстық спрей-пиролиз қондырғысын ұсынамыз. Дәстүрлі бір аймақты УСП қондырғыларымен салыстырғанда, бұл құрылғы «тамшы-бөлшек» түрленуін кезең-кезеңімен іске асырады, қуысты морфологияның түзілуін азайтады және прекурсор бөлшектерінің біртектілігін арттырады. 400-600 °C диапазонында алынған $LiFePO_4$/C ұнтақтары бастапқы (шашыратылған) күйде әлсіз кристалды немесе жартылай аморфты құрылымға ие болды, ол аргон атмосферасында 600 °C температурада 3 с бойы күйдіруден кейін фазалық таза оливин $LiFePO_4$-ке айналды. СЭМ зерттеулері көрсеткендей, УСП арқылы тікелей алынған бастапқы бөлшектер сферикалық, субмикронды (~200 нм-1 мкм) және тегіс беткейлі болып табылады, ал кейінгі күйдіруден кейін морфология сақталғанымен, беткей құрылымы іріленіп, қуыстар пайда болды. Мұндай микроструктуралық өзгерістер тығыздық пен Li^+ иондарының тасымал жолдары арасында теңгерім қалыптастырады, бұл бұрынғы УСП арқылы алынған $LiFePO_4$/C деректерімен сәйкес келеді. Екі фазалы саптама және жалын шашыратқыш пиролиз жүйелерімен салыстырмалы талдау біздің қондырғымыздағы градиент термиялық бақылау мен электростатикалық тұндыру үйлесімі алынған ұнтақтардың сапасын жақсартатынын және зертханалық дәлдік пен әлеуетті масштабтаудың перспективті комбинациясын қамтамасыз ететінін көрсетеді. Бұл нәтижелер арнайы жасалған УСП әдісінің морфологиясы мен кристалдық құрылымы бақыланатын жоғары сапалы $LiFePO_4$/C катодты ұнтақтарын алуға тиімді әрі икемді платформа екенін дәлелдейді.

Түйін сөздер: литий темір фосфаты ($LiFePO_4$), катодты материалдар, ультрадыбыстық спрей-пиролиз, алты аймақты пеш, морфологияны бақылау, литий-ионды аккумуляторлар.