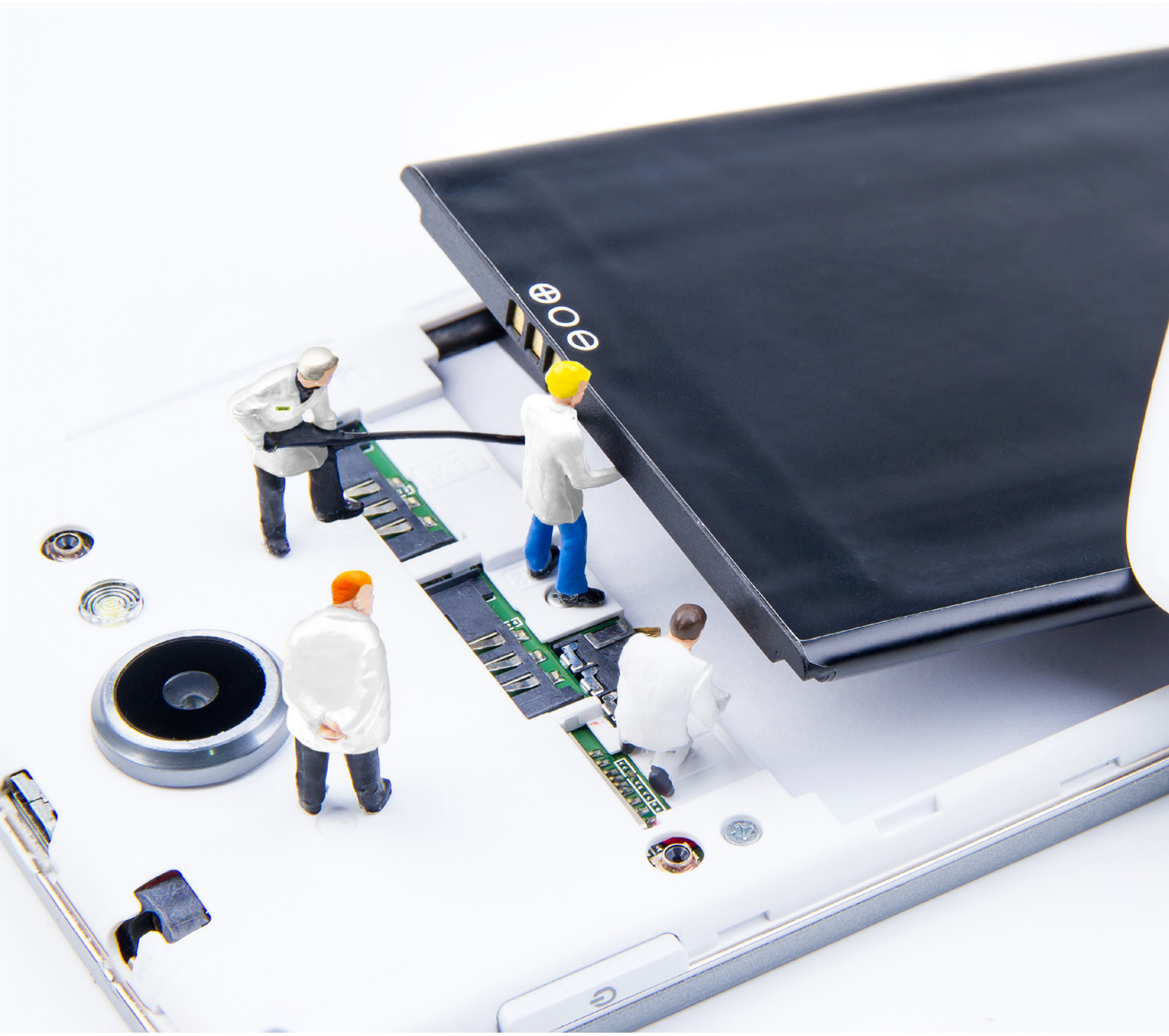
# Graphene-based composites for lithium batteries by spray drying



## 1. Introduction

Graphene, a thin, hexagonal lattice material, has attracted a great deal of research interest since it was first reported in 2004 by Andre Geim and Konstantin Novoselov at the University of Manchester. The two researchers were awarded the Nobel Prize in Physics in 2010 for their work. Graphene has many interesting features such as high electric conductivity, superior mechanical properties, excellent chemical tolerance, and high surface area.[1] The theoretical specific surface area is 2630 $m^2/g$ which is much larger than carbon black (typically smaller than 900 $m^2/g$) or carbon nanotubes (from 200 to 1000 $m^2/g$).[2]

Graphene serves as a functional composite for rechargeable Li-ion batteries (LIBs). LIBs are commonly used as energy storage systems, however, they exhibit a relatively low electric conductivity and have a short life cycle.[3] In order to improve the performance of Li-ion batteries, research has focused on the development of both anode and cathode materials. Various graphene-based composites have been developed, such as $TiO_2$/ graphene, $Co_3O_4$/graphene, $SnO_2$/ graphene, $Co(OH)_2$/graphene, $Mn_3O_4$/graphene, $Li_4Ti_5O_{12}$/ graphene, $Fe_3O_4$/graphene, $LiFePO_4$/graphene and others [1,7], that show superior performance to current anodes.

Spray-drying is a simple, affordable, easily scalable technique that enables control of particle size and morphology. Because of this, spray drying has been widely used for synthesis of functional nanoparticles or special structures in the field of chemical engineering and advanced materials. In this adviser, the important steps needed to obtain graphene-based composites using the BUCHI Mini Spray Dryer will be highlighted.

## 2. Spray drying of graphene-based composites in the LIBs fieldeld

LIBs consist of three primary functional components: a positive electrode, a negative electrode and electrolytes. The electrochemical roles of the electrodes reverse between anode and cathode, depending on the direction of current flow through the cell.

With the discovery of single layer graphene sheets, graphene-based electrodes have been tested for optimization of LIBs. For example, Yuan et al. constructed three dimensional crumpled graphene sheet-wrapped nano-$Li_4Ti_5O_{12}$ (LTO@GS) composites as anode material to improve the electric conductivity and power capability of LTO.

Graphite oxide was first synthesized from natural graphite powder using a modified Hummer's method, then it was exfoliated into deionized water by sonication to form a graphene oxide (GO) suspension. This sample was dried on the spray dryer as a final step (Figure 1).[3]

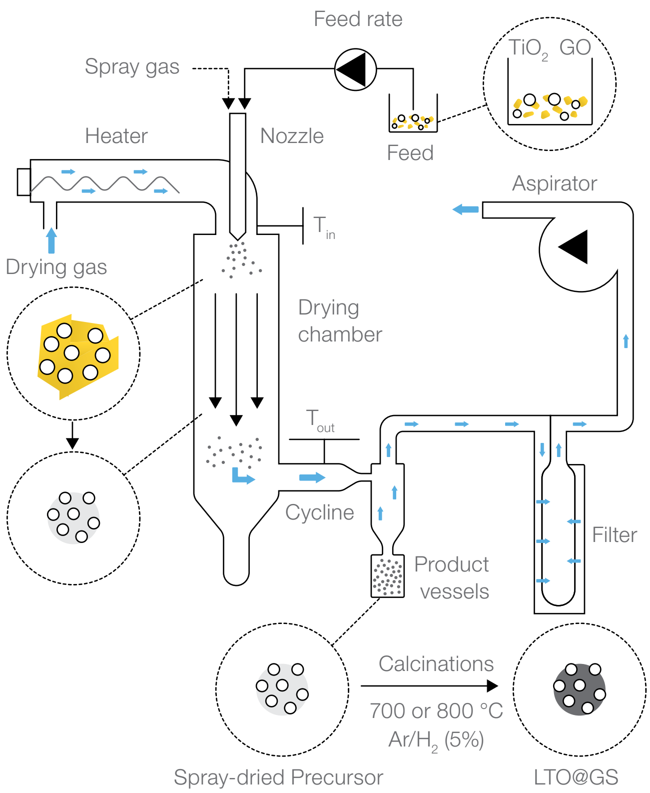



Figure 1: Schematic of the synthesis route of LTO@GS composites.

Wang et al. fabricated a porous pyrolyzed polyacrylonitrile-sulfur@graphene nanosheet (pPAN–S@GNS) through spray drying as new cathode material for the next generation of LIBs. The spray drying process was shown to assemble PAN and GNS in such a manner that GNS is loosely wrapped around the mono-disperse PAN nanoparticles. GNS inside the microspheres presumably integrate into a continuous conductive network, resulting in superior rate capability and excellent cycling stability for cathode material.[4]

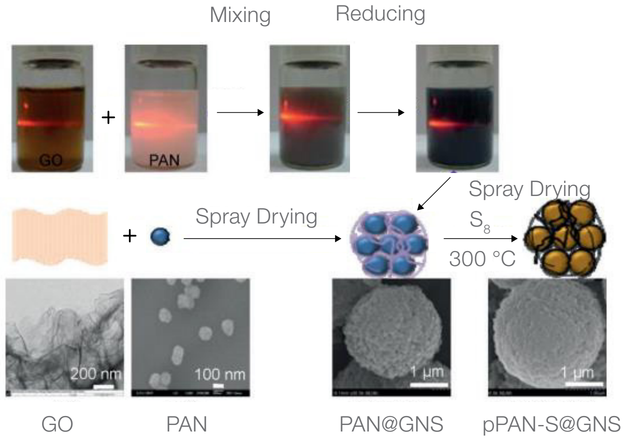



Figure 2: Schematic of the synthesis pPAN–S@GNS process, including production of the spherical nanoporous PAN@GNS precursor material and pyrolysis to form the final composite.

Spray dryers have been used extensively to investigate a number of powdered products and can be used to tune product structure. Spray drying parameters, such as temperature, concentration, pressured gas, inital particle size etc, affect the morphology of the final particle.[5] This technique could be used to convert planar structure to three dimensional (3D) structure under compressive forces and rapid droplet evaporation. As the drying process continues, more ripples appear on the droplets' surface and the wrinkled surface is compressed. Therefore, in the LIB field, materials such as $TiO_2$, $Co_3O_4$, $Li_4Ti_5O_{12}$, $LiFePO_4$ were encapsulated within the crumpled particle to produce graphene-based hybrids.The graphene composite could help to improve the LIBs' cycling performance, electrial conductivity, (dis)charge rate capability and also effectively buffer the volume change of the functional particles.[1]

## 3. Recent research with spray drying instruments

| Powder produced | Function | Spray drying instrument & parameters |
|---|---|---|
| $Fe_2O_3$@graphene sheet [6] | Anode material for LIBs | Mini Spray Dryer B-290 $T_{in}$ 220 °C |
| $Li_4Ti_5O_{12}$@graphene sheet [3] | Anode material for LIBs and electrochemical capacitors combine system | Mini Spray Dryer B-290 $T_{in}$ 200 °C |
| Pyrolyzed polyacrylonitrilesulfur@graphene [4] | Cathode material for LIBs | Mini Spray Dryer B-290 $T_{in}$ 220 °C |
| Micrometer-sized graphene oxide [2] | Electric double-layer capacitor | Mini Spray Dryer B-290 $T_{in}$ 120 °C; $T_{out}$ 80 °C; Aspirator 100 %; Feed rate 2.74 mL/min |
| Graphene oxide-Si [1] | Anode material for LIBs | - |
| $LiFePO_4$/graphene microspheres [8] | Cathode materal for LIBs | - |
| Si/graphite@graphene [9] | Anode material for LIBs | - |

*$T_{in}$ is the inlet temperature of spray dryer, $T_{out}$ is the outlet temperature.

Table 1: Summary of recent research using spray drying to produce graphene based particles

## 4. Conclusion

The spray drying technology is widely used in advanced material research. Graphene as a newfound material with excellent characteristics has been used in LIBs production either in the anode or in the cathode since 2004. Thanks to long time experience in spray drying, BUCHI could provide reliable and professional laboratory support and solutions for customer research. Lab-scale spray drying with BUCHI instruments can be easily scaled-up according to well-known transfer parameters, for easy transfer from lab to production scale.

## References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