Spray dried nano oxide ceramics for free flowing plasma spray coating powders and battery material processing

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Abstract. Advanced materials are widely used in electronics, aerospace and automobile industry devices and also in substances synthesized for food, medical and pharmaceutical industries. The quality of the base material powder has high influence on the resulting material body (the product) which goes into the manufacture of the device. To name a few (a) flowable ceramic powders from agglomerated nano ceramic powders for plasma spray coatings with the right sprayable powder characteristics (b) advanced graphene encapsulated nano ceramic oxide powders with uniform conductive coating layers as promising electrodes in Li-Ion batteries, (c) advanced bio-ceramic oxides such as hydroxyapatite ceramic materials with right amounts of moisture, density and composition consistency as bone and dental implants in bio-ceramics research are examples. Among the many processing methods to achieve the base powders from nano ceramic raw materials the most capable and efficient is ‘Spray Drying’ which results in powders with high purity with well-defined properties. Complex composite by spray drying is achieved where the ‘matrix host’ material is encapsulated by the ‘guest layer’ with special properties. This paper illustrates results pertaining to experimentation via spray drying and microscopic investigation by using SEM associated with EDS on (a) Yttria stabilized zirconia plasma sprayable powders for Thermal Barrier Coatings application and (b) nano yttria stabilized zirconia incorporated into microns sized alumina powders for enhanced densification, to understand the significant role of process parameters on uniformity and consistency of the spray dried products. Information based on review on spray dried Li-ion battery materials is also included.

1. Introduction

Nano-materials have a cutting-edge position whenever the scientific materials community embarks on a program to develop materials with unique and specific features. The functionality offered by such class of materials promise custom-made role for dedicated applications in many vital and high technology application industrialized segments. Nano-materials involve material resources of which minimum one measurement of its size is in the nano-scale (1nm to100 nm), that is, made up of nano scale divisions. Materials like nano-particles, nano-tubes, nano-rods, nano-wires, nano-films, compacted nano-structured products, and nano-porous materials are members of this family. [1]
Nano-materials became attractive to the scientific world due to their peculiar physical and chemical properties. Some of the special characteristics a nano material possesses include unique surface characteristics, superiority due to dimensional manifestations, quantum and tunnelling effects that make these materials totally alien to the everyday engineering products. These characteristics guide towards development of numerous new applications and some of them are listed below: [2–4].

Automotive and aerospace industries: Some of the advanced products a nano technology can bring about includes tyres reinforced with nano particles, body materials strengthened with nano particles for light weight, external painting of the bodies to get interactive surfaces, development of non-flammable plastic materials; electronics items for controls, self-repairing or healing coatings, thermal barrier coatings on high temperature parts to protect the surface or increasing the life span and textiles having special characteristics.

Electronics and communications: Some of the advanced capabilities brought by nano technology includes, use of nano layers and dots in media recording devices, developments in wireless technology, development of latest gadgets and process activities in the field of ICT (Information and communication technologies) and many new capabilities in the field of electronic circuits.

Pharmaceutics, health-care and life-sciences: One of the main controlling factors in the interaction between two materials is its surface area. The huge surface area available to the nano materials makes its properties different from its conventional materials. This property is used in the synthesis of unique nano-structured drugs, gene and drug delivery systems; bio compatible substitutions in human anatomy and bodily fluids; material used to treat bones and enable tissue regeneration; blood replacement etc, nano robots for the treatment of tumors and replacement of surgery.

Energy: Potential use of nano-materials in the energy field include new types of high capacity and high-performance batteries, technology for artificial photosynthesis for clean energy, light-weight materials and tinier circuits for energy saving, light-weight space vehicles, create economical sources of power generating and managing scenario, miniature and competent robotics.

Thus, nano materials play a very significant role in the world of devices that include powder preparation methods especially in the nano scale. It is in this regard the background of this paper is set with focus on the importance of the apt usage of spray dried nano powders.

It must be understood that mere synthesis of nano powders by the well-known processing routes such as sol-gel, co-precipitation, attrition milling is not sufficient to be directly put under use in applications involving special devices etc, especially when compounds or coatings with specific properties are desired to be synthesized. Furthermore, nano powders by themselves have the tendency to agglomerate randomly and without control and that make them sticky and not flowable. Therefore, it may be beneficial to agglomerate the nano-powders in a controlled manner so that the nano dimensions of the particles are retained in-toto, and yet the micron sized agglomerated nano particles may be converted into free flowing powder so that they may be used as the feedstock of plasma spray coatings or in drug delivery systems or even paints and emulsions etc. Spray drying is an important process methodology and instrument that can be used to agglomerate nano powders to suitable micron sized powders to serve the purpose.

1.1 Role of spray drying as a tool to synthesize smart materials

Though many methods are available to produce the nano sized powders, spray drying is the most common process to produce high quality materials of the uniform morphology. In a spray drying process, the solid material of the required particle size is separated from the solution or the liquid containing the suspended particles using the equipment called a spray dryer. The liquid is sprayed in to a drying chamber as very tiny droplets and the drying is achieved by the passage of hot gases. The nature and the temperature of the gas are decided by the raw material and the quality of the product.
The binders used for spray drying and the spray parameters play a major role in the final product i.e. the spray dried powder.

Granulation and controlled agglomeration are two of the processes which can be achieved using a spray dryer. Granulation refers to the process of the formation of granules out of fine particles. Granules of the required micron size are achieved by mixing the raw material with suitable binders and dispersants and subsequent spray drying. In the case of plasma sprayable powders, nano materials will not flow smoothly to the plasma jet and may agglomerate/stick in the flow line to produce coating issues. Particles of nano size also will expose health issues due to the fine size and chances of suspension in the air. These nano particles are agglomerated using suitable binders in a spray dryer. The low melting binders will evaporate during the transit through the high temperature plasma and only the semi molten nano sized ceramic particles will be deposited on the target.

In this work, nano powders (10 to 50nm) of 8% Yttria Stabilized Zirconia (commercial sources) commonly known as 8YSZ, popularly used as Thermal Barrier Coating Materials feedstock in Atmospheric Plasma Spraying (APS), were used as the starting raw material and they were spray dried to be synthesized in free flowing agglomerates by employing spray drying technique.

2. Experimental work

2.1 Spray drying of nano ceramic powder:

The experimental work conducted in the lab to synthesize the ceramic powders using spray drying process and the process routes to achieve them and to ensure the quality is explained below. Figure 1 shows the photograph of the spray dryer system used in the present work. The spray dryer unit typically consists of drying parameter controls, drying chamber, cyclone, compressor for air supply etc. Accessories used in the spray drying process comprise of weighing balances, ultrasonic cleaner, magnetic stirrer etc. The details of the lab scale spray dryer used are the following.

Type: Laboratory Scale
Manufactured by: Technosearch Instruments, Mumbai
Capacity: ~ 300 to 500 g based on solution type and concentration
Time to process one batch: ~ 4 hours
A typical synthesis of nano ceramic powders starts with the slurry or solution in a beaker with a suitable binder (typically polyvinyl alcohol i.e. PVA for engineering applications) where the particles are in the suspended form. A magnetic stirrer keeps the particles in the suspended from throughout the spray drying process. Bio-medical implant materials etc. require binders of highly specific compositions that are of non-reactive nature with the human body. Air supplied by the compressor and a sensor controlled heater unit will keep the drying chamber at the required temperature level. Controlled amount of liquid is sprayed into the drying chamber based on the required properties of the powder and particle size. The liquid will be evaporated and the powder of the required particle size is collected in the collector bottle below the conical section of the drying chamber. Very fine powders which are smaller than the required particle size will be carried away by the current of the gas (generally air) and will be collected in cyclones. These fine powders can be recycled till we get the required particle size. A closer view of the drying chamber during the spray drying process is shown in figure 2 and the sprayable powder collected from the chamber is shown in figure 3.

![Figure 2. Drying chamber during powder collection.](image1)

![Figure 3. Collected spray dried powder from chamber](image2)

The agglomerated nano powders tend to stick to the drying chamber and get collected in the collection jar. The powders stuck to the glass walls may be brushed out of the chamber and collected, which are usually free flowing. The collected powders were found to be free flowing and highly suited as feed stock materials to serve as plasma sprayable powders.

2.2. Synthesis of nano composite powders via spray drying:

In order to synthesize dense composites, and for reducing the sintering temperatures of the product, the inter-particle spaces may be filled with nano particles of the same composition. For example, nano sized voids created within micron sized particles composites may be filled with nano particles for same composition such that the composition consistency remains unchanged. In this work nano grains of 8YSZ were used to fill the voids between the particles of 20 to 30 micron sized \( \alpha-\text{Al}_2\text{O}_3 \), with an attempt to study the distribution of the nano 8YSZ grains within the host matrix.

For the purpose, 0.5% of nano 8YSZ and 99.5% alpha alumina (\( \alpha-\text{Al}_2\text{O}_3 \)) were spray dried together by using PVA binder to make the suspension that was ultrasonicated for half an hour prior to spray drying. This exercise ensured uniform distribution of the nano particles in the slurry.
3. Characterization of the spray dried ceramic powders

The spray dried powders were analyzed for particle morphology and shape by employing Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) for assessment of chemical composition of the material and the uniformity in distribution as well. Figure 4 shows the SEM micrograph of the spray dried powder at (a) low magnification of 500X and (b) high magnification of 25,000X.

While the powder particles seen in Figure 4a do not reveal the presence of nano grains embedded on the surfaces of the micron sized Alumina, they are visible in Figure 4b. In order to confirm the uniform distribution of the nano grains, EDS analysis were carried out on several tens of particles chosen in a random manner and typical composition analysis results are shown in Figure 5.

As expected, the chemical composition of the spray dried particle revealed extremely small quantity of 8YSZ along with major fraction of Al₂O₃, confirming the success of the spray drying process. Yet two more results pertaining to particles analysed are shown in Figure 6 and Figure 7.
Comparing the typical data/results that are shown in Figure 5 thru 7, it is observed that yttrium content that originated from the dopant Yttria (Y₂O₃) varied between 0.5 and 0.6 weight %, which may be considered as a small margin and established the suitability of the spray drying process to dope a ceramic host material. It is evident that had the dopant been nano α-Al₂O₃ in a host of micron sized α-Al₂O₃, the nano grains would have been dispersed uniformly in the host matrix. This method of doping is expected to significantly improve the sintering characteristics of ceramics involved and reduce the sintering temperature as well.

To summarise, the findings on spray dried composites via spray drying nano 8YSZ with micron α-Al₂O₃, allowed us to bring out the significant manner in which the nano particles could be uniformly and consistently incorporated in a large host matrix comprised of particle dimensions that were micron sized.

This particular mechanism involving uniform dispersion of dopants in matrix plays a significant role in synthesis of battery electrode materials. This avenue is being explored further by performing review of battery electrode materials and to assess the suitability of spray drying in battery material processing.

**4. Review of the role of spray drying of Lithium ion battery materials for capacity enhancement**

A battery is a device which consists of one or more electrochemical cells that convert stored chemical energy into electrical energy. Though the invention of first electrochemical battery dates back to the year 1800, it underwent too many modifications and improvisations due to challenges in the field of...
material selection and processes to enhance the capacity and safety in the past two centuries and still it is continuing.

In the R & D of batteries, a major breakthrough happened in 1985 and started commercial production in 1991. Compared to the earlier family of high capacity batteries, Li-ion battery offered (a) higher energy density, (b) absence of memory effect which was limiting the capacity of earlier high power batteries like nickel-cadmium batteries and (c) negligible self discharge. Li-ion batteries use different anode - cathode- electrolyte combinations to control the characteristics and out-put of the battery.

The research to develop a high power high storage capacity battery, especially secondary type (rechargeable) has become extremely urgent and important due to the health issues posed by the pollution due to the traditional internal combustion (IC) engines and the efforts to find a substitute for it. The efforts for a clean air technology have resulted in the development of a number of automobiles using high power batteries for their propulsion. The main challenges in the field of electric cars are the development of high capacity, safe batteries at reasonable cost. The researches happening in the improvements of Li-ion battery by developing new smart materials for the anode, cathode and electrolyte combination are taking faster strides and has a huge potential of improvement. It is believed that the use of nano technology has the potential to develop newer materials which may offer tremendous improvement in the capabilities of the battery. One of the easy and practical processes to produce nano composites to enhance the capabilities of the battery electrodes is spray drying. Proper material combinations can be selected, spray dried and then processed to get the high performing electrode materials in Li-ion battery (LIB) components. A typical Li-ion battery consists of a) an anode b) a cathode and c) an electrolyte matching for the anode - cathode combination. The potential of spray drying in the development of anode and cathode materials is discussed in this paper.

4.1. Present status and future potential of spray drying

Advances in the battery technology research and products related expansion is the main target of the related industries. They heavily depend upon enhancements in the energy and power densities of the related materials and at the same time lessen the constraints imposed by volume and mass of the devices.

In traditional LIBs, crystallites of compounds with steady electrochemical potentials are employed to permit intercalations of the Li ion (chemical reaction in which Li or H2 is allowed to be introduced into a host matrix inter-layers and essentially by retaining the crystal structure)[5]. The most popular active cathode (positive electrode) material is lithium doped metal oxide and the most common active anode (negative electrode) material is graphitic carbon. The active materials are bound or agglomerated with binders like polyvinylidene fluoride (PVDF) and certain stabilizers that possess conductivity characteristics like carbon black, graphite etc., before proceeding to being introduced on current collectors that could be metallic foils. Polymeric separators are used to electrically insulate the cathode and anode in the LiB. A micro-porous polymeric (such as polypropylene/ polyethylene) laminate that permits lithium ion diffusion is a common separator material. Traditionally, the most popular active cathode materials that the most of commercial batteries have used are based on oxides of lithium and cobalt such as LiCoO2, while the active anode material are carbon based which may be graphite or meso-carbon micro-beads (MCMBs). In order to enhance the battery specific energy density (Wh kg⁻¹), on the whole the battery capacity (Ahkg⁻¹) along with the voltage (V) have to be increased [5]. The voltage of the device, i.e the battery is a consequent of the large electrochemical potential difference generated between the cathode and anode with respect to the Li-metal.

Most of the batteries use graphite as the anode and it has a constant potential between 0.1– 0.2V vs. Li/Li+. The battery voltage and storage capacity are highly influenced by the cathode chemistry, stoichiometry, and crystal structure of the material used. So, attempts to increase the specific energy density can be done by improving the cathode capacity and/or by increasing the voltage of the cathode
vs. Li/Li+. Other strategy to increase the energy density is to augment the anode capacity sufficiently to increase the number of active layers contained within an individual battery.

The development of nanostructured electrodes to address the limitations of bulk crystalline expansion can be envisioned by either decreasing the size of the semiconductor particles to the nano-scale or through introduction of other functional nano-materials. A reduction of a material’s particle size to the nano-scale (i.e. <100 nm) can change the crystal structure and may modify the mechanism of volumetric expansion upon lithiation.

At present, Li-ion batteries (LIBs) and electrochemical capacitors (ECs) are considered as the most common types of energy storage systems [6]. However, in the current scenario, neither LIBs nor ECs can meet the demands of practical applications. Several lithium-insertion type materials like LTO, TiO₂, NiCo₂O₄, LiTi₂(PO₄)₃, TiP₂O₇, LiCrTiO₄, and graphite have been proposed as a potential alternative host material.

In chemical engineering and materials field, the spray-drying technique has been widely used for synthesis of functional nano-particles or special core–shell structure encapsulation for mass production due to the simplicity in the apparatus and process and possibility for easy scale-up. When these materials are compounded with other functional materials like Graphene, layers can encapsulate functional materials simultaneously during the shrinkage process to form graphene-wrapped materials with entirely different special properties.

Graphene, the special two-dimension (2D) material, has recently attracted a great deal of research interest due to some of its peculiar properties like very good mechanical flexibility, superior electrical conductivity, huge specific surface area, and so on [8]. Graphene has been introduced into various organic and inorganic materials, as a modified component to form functional composites for LIBs.

The spray drying technique has been widely used successfully for nano-particle encapsulation in the chemical, pharma, and food industries due to its low cost, simple apparatus and the easiness to scale-up for mass production [8]. This technology could be a promising route for the mass production of various high-performance 3D crumpled graphene wrapped composites. In spray drying process, surfactant, filtration, washing and high vacuum conditions are not required. This is a safe and environmental friendly process. Graphene not only constitutes a good conducting network, but also provides enough void spaces and spray drying of battery electrode synthesis facilitates it.

Spray-drying method is considered to be a promising alternative way to synthesize oxide electrode materials with homogeneous and spherical morphology for lithium-ion secondary batteries. The precursor obtained by spray-drying method is found to be dense, and spherical with smooth surfaces.

5. Conclusion

The findings in this research work allow us to conclude that the term “spray-drying” method of powder synthesis covers many different features desired for base materials used for synthesis of plasma sprayable powders, dense ceramics and battery electrode materials. The reasons for using spray-drying are multi fold which include uniform distribution of dopants in a matrix, consistent powder characteristics and therefore enhanced product properties. In many cases, spray-drying is a laboratory-scale procedure to the next level in terms of production quantities, reproducibility, and control of agglomeration. This is true, for example, for many solid state reaction synthesis on the condition that the starting materials are not soluble in the liquid medium of the suspension. Moreover, it must be appreciated that, except in the presence of volatile compounds, all the material that is injected in the spray-dryer is delivered as spray-dried powder. It also offers new opportunities, such as the dispersion of carbon in active battery material without incorporating large composition in-homogeneities and is recognized in the industries involved in synthesis of electrode materials from lab- to pilot-scale quantities. One must be cautioned against the apparent effortlessness of the spray-
drying process. Several experiments, iterations and optimization are involved in the optimization of experimental spray-drying parameters which certainly affect the characteristics of the final product.

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