

The NanoSpray Process for Production of NanoStructured Carbon-Containing Materials

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Introduction

Nanostructured carbon-containing materials with high surface area are finding use in fuel cells [1-2], catalysis [3], batteries [4-6], and many other applications. A variety of preparation techniques have been reported for carbon-supported metal nanoparticles, including liquid suspensions [7], metal evaporation and carbon coating in low vacuum [8], and electrochemical deposition on carbon surface [9]. Spray systems are well known in industrial applications, wherein carbon particles can be made by fuel rich flame combustion systems or thermal cracking of hydrocarbon materials.

This paper describes the NanoSpray and combustion chemical vapor condensation (CCVC) process [10-11] in which spray or vapor can be used to form carbonaceous materials and combine them with inorganic materials to enable performance enhancement in electronics, sensing, energy storage, and other applications. nGimat uses the Nanomiser[®] device [12] for ultra-fine aerosolization of liquid solutions at high rates along with the CCVC process suitable for high volume production of nanoparticles. This atmospheric pressure flame process dynamically combines the production and incorporation of carbonaceous and inorganic/organic materials into a one-step process that eliminates the need for post treatment. Through control of the flame temperature, stoichiometry and flow configuration, reacted inorganic material can serve as nucleation sites for the growth of carbonaceous material or can be inter-dispersed with or on the carbon-formed material.

Experimental

The experimental apparatus consists of the Nanomiser[®] device, which produced ultra-fine spray, surrounded by an annular gap for the oxidizer dispersant and pilots for combustion support. The precursors for the carbonaceous and inorganic materials and optional hydrocarbon fuel are supplied to the Nanomiser device using an HPLC pump (Shimadzu LC-10AT) at concentrations between 0.1 M and 2 M. The precursor flow rate can be varied from 3 to 100 mL/min and the resulting spray mean droplet size can be varied from 30 μm to $< 1 \mu\text{m}$ independently from the oxidizer flow rate. The atomized precursor is mixed with a coaxial flow of O_2 generating diffusion flame supported by premixed pilots. When larger droplets are used, the combustion heat vaporizes the solvent

exposing small clusters of the precursors, which then decompose to form particles. When small ($<1\ \mu\text{m}$) droplets are used (typical for the NanoSpraySM process), then the CCVC occurs from high surface area droplets, which are metastable in an energetic environment. The ensuing flash vaporization into reactive species results in rapid reaction and condensation of the nanopowders. The NanoSpray and CCVC processes enable simultaneous synthesis and intermixing of carbonaceous and inorganic nanomaterials.

Results and Discussions

Carbonaceous materials are produced utilizing the described NanoSpray process apparatus. A hydrocarbon fuel solvent was pumped through the Nanomiser device resulting in formation of fine aerosol that was ignited using pilot flames of premixed methane and oxygen. A coaxial flow around the spray provided oxygen needed. Ultra-fine water mist was used to uniformly and rapidly quench the hot combustion products and carbon black particles produced in the flame hot zone. Application of very fine water spray resulted in a more uniform and more rapid quench and production of more uniform and finer carbonaceous materials. Samples of carbonaceous material were collected on glass fiber filters and analyzed using transmission electron microscopy. Figure 1 shows the TEM image of a typical carbon black material produced in this example.

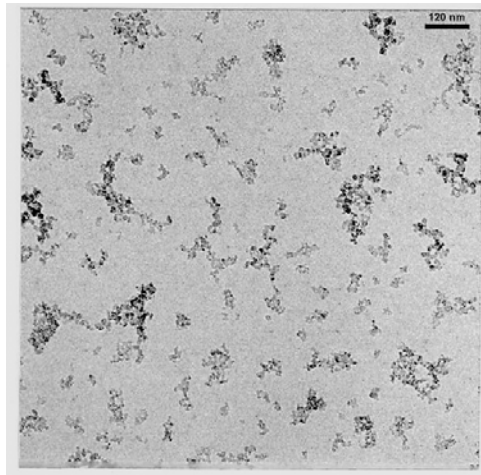


Figure 1. Carbonaceous nanoparticles produced using the NanoSpray process

Composite particles of polymer, carbon black and magnetite materials were also produced using the NanoSpray process. In this example, feedstock consisting of mixed hydrocarbon fuels was pumped through the primary Nanomiser burner and partially combusted to produce carbon black and hot combustion products. The resulting plume of hot combustion products and carbon black was mixed with the aerosol produced by atomizing polystyrene solution in acetone and cyclohexane. Polystyrene feedstock granules were dissolved in a 50/50 by weight mixture of acetone and cyclohexane to form a 2.5 wt% solution of polystyrene. Ten g per liter of magnetite was added to the solution with stearic acid to help suspend the iron oxide particles. The polymer containing aerosol

droplets were heated in the chamber by the gases from a carbon-producing flame. This resulted in production of spherical polymer particles containing carbon black and magnetite and coated with carbonaceous material. Figure 2 shows SEM micrographs of spherical and smooth polystyrene particles. Carbon black particles can also be seen covering the polymer spheres. Measurement of particle size from SEM micrographs indicates diameters of about 2 to 8 μm .

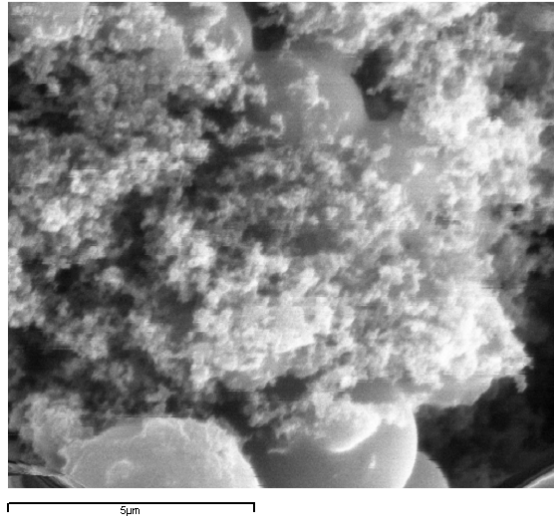


Figure 2. Polymer micro-particles containing inorganic nanoparticles and coated with carbonaceous material

Capabilities to nano-engineer carbon morphology have been applied to lithium primary batteries. Efforts to improve lithium thionyl chloride battery performance are ongoing by tailoring the cathode microstructure for NanoSpraySM-prepared carbon-Teflon composite cathodes. A CCVC system was modified and adapted for co-deposition of the composite materials structure, including modifications of a mixing chamber in which flame generation of active material is controlled while mixing occurs with polymeric components downstream. The CCVC/NanospraySM process exhibited the versatility to address the needs of both thick cathode layers for active primary (continuous discharge) cells and thin composites for high power density reserve batteries. Figure 3 shows comparative SEM cross sections of layers prepared using different processing parameters indicating the adaptability of the technique to deposit different electrode morphologies. Different Teflon slurry flow rates were used to introduce the polymer into the process stream which can create a denser (a, b) or more diffuse (c, d) microstructure.

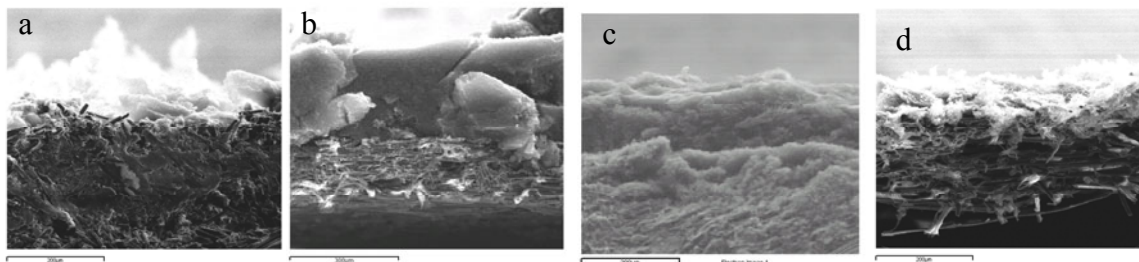


Figure 3. SEM images of electrode layers prepared using different NanoSpray processing parameters

The initial battery results show that 0.008” thick active cathode coatings, prepared by nGimat, can produce specific capacities of 28 Ah/g C at a medium rate (continuous) discharge for active primary batteries, more than ten times that observed at this rate with conventional cathodes used for this battery chemistry. The performance and manufacturing throughput enhancements obtained using the CCVC and the NanoSpraySM techniques for producing carbon-catalyst-Teflon lithium oxyhalide cathode composites are currently being optimized.

In a related PEM fuel cell research efforts at nGimat, we have demonstrated the ability to attain composite supported electrocatalyst layers in a one-step process. Figure 4 shows a transmission electron microscopy image of the nGimat prepared carbon supported platinum electrocatalyst layer.

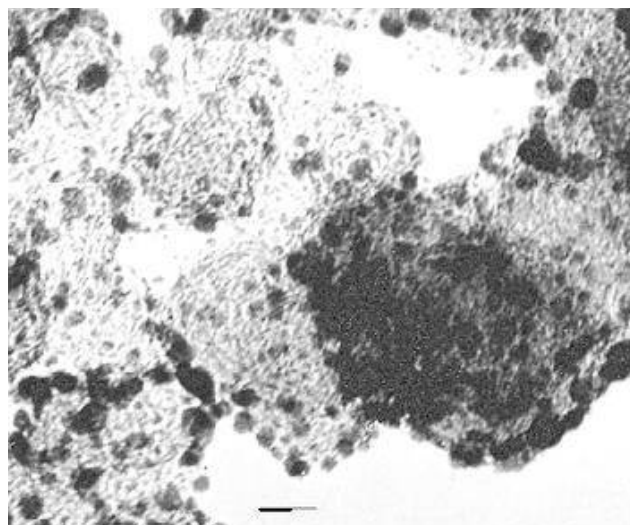


Figure4. High resolution transmission electron microscope image of nGimat platinum (darker specks) supported on carbon (Vulcan XC-72, lighter gray tone). Scale bar reads 10 nm.

It is evident that 2-8 nm size Pt particles can be supported on the carbon allowing for high catalyst surface area. Additionally, we have demonstrated superior oxygen reduction performance relative to commercially available

Johnson Matthey materials. From these data, it is evident that the NanoSpray process prepared materials show superior performance at lower precious metal loadings. This is attributed to a more porous microstructure produced by the NanoSpray process, which is essential for improved mass transport performance and pore utilization. nGimat has also used the CCVC technique to produce platinum based alloys such as PtCo_{0.5}Cr_{0.5} and PtRu by controlling the deposition atmosphere an establishing reducing conditions at the Nanomiser® device. The ability to control deposition atmosphere and temperature is important in working with easily combustible materials such as macrocyclic ligand transition metal complexes which are important in thionyl chloride cathode electrocatalysts. These compounds have successfully been pyrolyzed and supported on carbon black.

Conclusions

The CCVC/NanoSpray process, utilizing an ultra-fine spray with a controllable droplet size, has been used to generate carbon-containing nanomaterials from inexpensive and easily handled liquid precursors at high rates. The CCVC technology is not material specific, scales readily and enables the production of nanoparticles with controlled composition, size, and morphology. The NanoSpray process offers high potential for one-step fabrication of carbonaceous nanomaterials as may be used for catalysis, fuel cells, electronics, sensors, and energy storage.

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