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CONTINUOUS, RAPID PRODUCTION OF UNIFORM MICROPARTICLES BY ELECTRODISPERSION

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Ultrafine particles constitute the key building blocks for diverse advanced structural and functional materials, such as high-performance ceramics and alloys. These advanced materials have tremendous impact in many areas, including catalysis, separations, electronics, energy production processes, and environmental applications. Of particular importance, nanophase ceramic or metallic materials that contain nanosized (<100 nm) particles/grains show dramatically improved performance (mechanical, electrical, optical, magnetic, and/or catalytic). The characteristics of ultrafine particles (i.e. size, morphology, monodispersity, purity, and homogeneity of composition) directly determine the properties of the materials that are made from them. Thus, the future application of advanced materials depends strongly on the capability to produce particles with outstanding characteristics.

Currently, there is a need for more efficient methods of production of high-quality ultrafine inorganic particles. Ideally, we desire an instantly reactive, continuous process that generates homogeneous ultrafine particles with controllable characteristics. The primary current technologies for synthesis of ultrafine particles are liquid-phase chemical and sol-gel processing, and gas-phase condensation. Most of the production processes for both approaches are conducted in batch mode. Gas-phase reactions typically require extreme conditions such as high vacuum and high temperature and give very slow particle production rate. A few continuous, liquid-phase processes have been developed for production of microspheres from alkoxide precursors (such as tetraethyl orthosilicate, TEOS); however, these involve relatively slow kinetics during hydrolysis and condensation, typically 30 minutes or more reaction time (Ogihara et al. 1995). In contrast, metal (such as Zr, Ti, Al, etc.) alkoxides are so reactive that agglomerated solids, rather than dispersed particles, are formed under conditions with rapid reaction kinetics. Thus, controlled hydrolysis/condensation

of alkoxides in a batch reactor (see, e.g., Matijevic, 1993; Li and Gonzalez, 1996) is the usual approach in the literature for the production of monodispersed metal oxide precursor powders. Tubular-type reactors have been designed for the *continuous* synthesis of ultrafine ceramic particles (such as titania and ferric oxide) via hydrolysis and condensation of metal alkoxides (Ogihara et al. 1997, Kubo and Yonemoto 1997). In addition, liquid spraying techniques including electrostatic spraying/atomization (Slamovich and Lange 1988, Kim 1995) and ultrasonic spraying (Janaćković et al. 1997) of liquids into gas have been used in ceramic particle production.

Electrodispersion technologies show promise for the production of inorganic microparticles. Harris and coworkers recently demonstrated the capabilities of the electric dispersion reactor (EDR), a multiphase electrodispersion precipitation reactor (Harris et al. 1990, 1995). That technology employs electric fields to atomize aqueous solutions into a immiscible organic liquids to form reactive microdroplets in the size range of 0.1 to 10 micrometers. The EDR has been employed, using metal alkoxide and metal salt solutions, to synthesize ceramic precursor powders (including silica, alumina, zirconia, and 1:2:3 yttrium-barium-copper). The EDR has been shown to be a viable means for production of microspheres and porous spherical shells; however, the particle size distributions of the products are generally quite broad.

This paper presents a new approach to particle production by electrodispersion. In contrast to the EDR, in which the electrodispersion creates microdroplets in immiscible liquid systems, this approach employs electrohydrodynamic flows for rapid and efficient mixing of miscible reactive fluids. The rapid homogenization reduces concentration gradients during the particle-production reactions, allowing the continuous production of homogeneous submicron particles under fast reaction conditions.

The capability of this method for rapidly and efficiently mixing miscible reactive fluids is illustrated visually in Figure 1, which shows representative results obtained for an example system of butanol containing a fluorescent dye being injected into a flowing stream of deionized water. With no voltage applied, dispersion and dissolution are relatively slow, while with increasing voltage, much more rapid and intense micromixing is achieved. This method may be applied to a wide variety of fluids; in principle, nearly any fluid may be used as the injected fluid, while the continuous fluid is limited to liquids of low enough conductivity that significant Ohmic conduction does not occur; for example, deionized water is an effective continuous fluid, while tap water is not acceptable due to electrolysis, high current, and poor generation of electrohydrodynamic flow. Better performance is expected for continuous fluids having high dielectric constant and low conductivity; deionized water, ethanol, other alcohols, and their mixtures have proven to be suitable fluids.

The results of representative experiments for a sol-gel reaction system, in which the two key reactants are metallorganic precursor and water, are presented. The experiments demonstrated that electrohydrodynamic micromixing can be used to overcome the challenges posed by rapid reaction kinetics in a metal alkoxide system. As seen in Figure 2, for results of the same chemical system at two different reactant concentrations, submicron particle size is controllable through variation of reactant/fluid ratios. The hydrous zirconia particles produced are relatively dense and nearly spherical, and there is a narrow size distribution. An effect of applied voltage on product quality was also apparent. At lower voltages, corresponding to lesser uniformity of the reactant mixture, there is greater variation of particle size and increased particle agglomeration. With increasing voltage, particle size is decreased and particle uniformity is increased. It was noted that the particle suspensions produced at higher voltages were more stable; for example, the particles produced at 500 volts settled within 30 minutes, while the sol produced at 8000 V was stable for several days.

It has been demonstrated that it is possible to use electrohydrodynamic micromixing to continuously produce non-agglomerated, monodispersed, submicron-sized, sphere-like powders by controlling the reaction and spraying conditions. The size and homogeneity of product can be controlled through selection of reaction conditions, including reactant concentrations and injected and continuous fluid flow rates. A correlation between spraying voltage and the particle size, homogeneity, and sol stability was observed. These positive results indicate that this method could be used to dramatically improve advanced materials production. The approach offers the following potential advantages compared to classical batch synthesis: (1) faster particle production rate, (2) continuous production, (3) higher solids fraction with higher initial reactant concentration, (4) stable ultrafine particle product, and (5) controllable monodisperse size.

References

M. T. Harris, W. G. Sisson, S. M. Hayes, S. J. Bobrowski, and O. A. Basaran, "Porous Spherical Shells and Microspheres by Electrodispersion Precipitation," *Mat. Res. Soc. Symp. Proc.* **372**, 43 (1995).

M. T. Harris, T. C. Scott, O. A. Basaran, and C. H. Byers, " Morphology Control in Precursor Ceramic Powder Production by the Electrical Dispersion Reactor," *Mat. Res. Soc. Symp. Proc.* **180**, 153 (1990).

D. J. Janaćković, V. Jokanović, L. J. Kostić-Gvozdenović, S. Zec, and D. Uskoković, "Synthesis and Formation Mechanism of Submicrometre Spherical Cordierite Powders by Ultrasonic Spray Pyrolysis," *J. Mater. Sci.*, **32**, 163 (1997).

K. Kim, "Fabrication of Glass Micro- and Nanospheres from Liquid Precursors using Droplet Generation and Sol-Gel Processing," *Mater. Res. Symp. Proc.* **372**, 25 (1995).

M. Kubo and T. Yonemoto, "Continuous Synthesis Process of Large-Sized Titanium Dioxide Fine Particles Using Two-Stage Slug Flow Tubular Reactor," *1997 AIChE Annual Meeting*, Paper 157e, November, 1997, Los Angeles, USA.

B. Li and R. D. Gonzalez, "Sol-Gel Synthesis and Catalytic Properties of Sulfated Zirconia Catalysts," *Ind. Eng. Chem. Res.* **35,** 3141 (1996).

E. Matijević, "Preparation and Properties of Uniform Size Colloids," *Chem. Mater.* **5**, 412 (1993).

T. Ogihara et al., "Continuous Synthesis of Monodispersed Silica Particles Using Couette-Taylor Vortex Flow," *J. Ceram. Soc. Japan* **103**, 151 (1995).

T. Ogihara, M. Yabuuchi, T. Yanagawa, N. Ogata, K. Yoshida, N. Nagata, K. Ogawa, and U. Maeda, "Preparation of Monodispersed, Spherical Ferric Oxide Particles by Hydrolysis of Metal Alkoxides Using a Continuous Tube-Type Reactor," *Adv. Powder Technol.* **8**, 73 (1997).

E. B. Slamovich and F. F. Lange, "Spherical Zirconia Particles via Electrostatic Atomization: Fabrication and Sintering Characteristics," *Mater. Res. Symp. Proc.* **121**, 257 (1988).

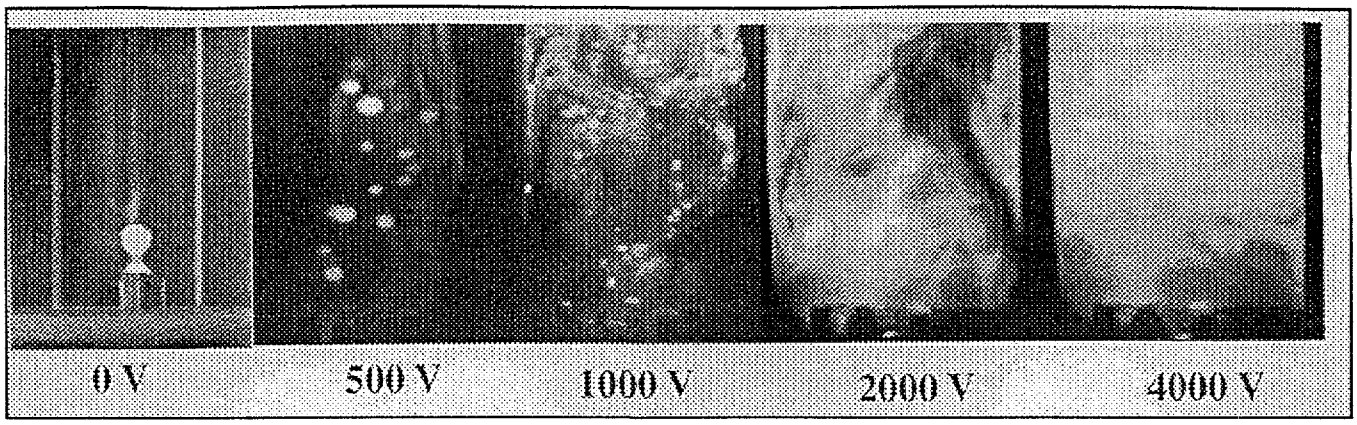
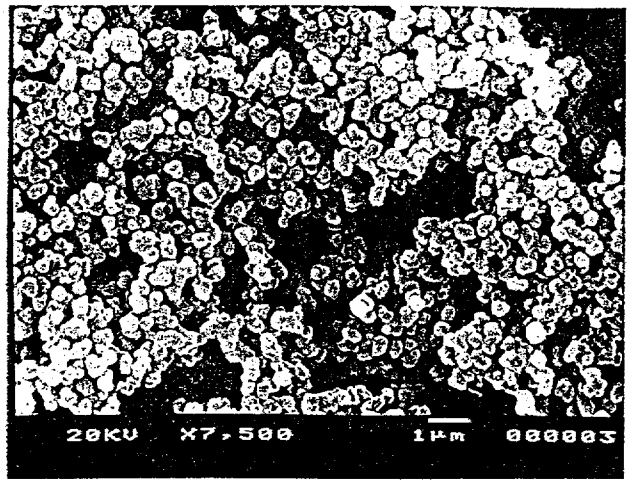


Figure 1. EHD mixing of butanol in deionized water. Conditions: butanol - 0.8 mL/min, water - 50 mL/min, tube i.d. = 7.5 mm.



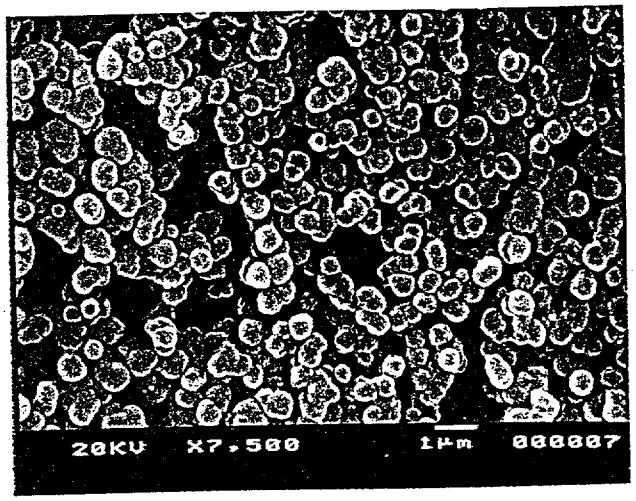


Figure 2. Hydrous zirconium oxide particles prepared by electrohydrodynamic micromixing