From Pottery to Membranes:
Characterization of Ceramic Powders and Surfaces

Relevant for: ceramics, laser diffraction, DLS, ELS, zeta potential, particle size distribution, streaming potential, PSA, Litesizer, SurPASS

Defined properties and high quality of ceramic products rely on precise and accurate characterization of raw ceramic powders, slips and final ceramic products regarding key parameters including particle size, particle size distribution and zeta potential. The PSA and the Litesizer series enable reliable, fast and easy particle size measurements in a broad range. The zeta potential of ceramic powders and bulk bodies is determined most accurately with Litesizer 500 and SurPASS 3, respectively.

1 Introduction

Ceramics are inorganic non-metallic compounds, which have been shaped and then hardened by heat treatment. The term covers a large group of materials with a wide variety of chemical compositions and applications. Based on their chemical composition ceramics can be categorized as oxide ceramics like alumina and non-oxide ceramics such as nitrides, borides or carbides. Ceramics are also classified as traditional and advanced or high-performance ceramics. Advanced ceramics are distinguished from traditional ones by their outstanding properties not only in the mechanical field (e.g. strength, operating temperature, toughness, workability etc.), but also by special properties such as piezoelectricity or conductivity. Advanced ceramics are also characterized by the hardening process, which often requires extremely high temperatures (1).

Production of ceramics generally consists of a series of steps: The preparation of the raw powders, also called powder processing, includes crushing and grinding to the desired size range and chemical treatments to separate phases and compounds. The optimal final powder has to meet strict quality expectations, and is therefore regularly characterized in particle size distribution and shape (Figure 1).

During the forming process the powder is consolidated into the desired shape either by pressing or, mixed with water and additives, by molding, creating the so called green body. A following drying step is required to avoid cracking that would be caused by the rapid evaporation of water during sintering. The sintering or firing might be a multi-step process in itself, consisting of pre-sintering resulting in a brown body, and a main sintering step, which generates the final product, also called the white body (Figure 1).

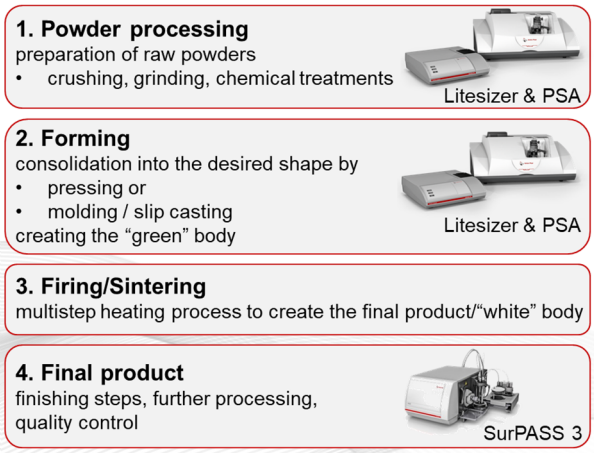

Figure 1: General and simplified overview of ceramic processing steps

A prominent application for high performance ceramics are ceramic membranes. They are porous or dense artificial membranes used for liquid filtration or gas separation. Due to their typical ceramic properties they can be formed in any shape and withstand aggressive media or extremely high temperatures.

In this application report we demonstrate how the Anton Paar instruments for the characterization of particle sizes and surface charge can contribute not only to the development of new slip mixtures, but also to the regular quality control of raw powders and the surface characterization of final products.

2 Experimental Setup

Independent ceramic samples were characterized regarding particle size distribution and zeta potential. Laser diffraction measurements were performed with the PSA 1190LD, and dynamic light scattering (DLS) experiments with the Litesizer 500 in order to determine particle size distributions of ceramic raw powders and a premixed slip suspension.

Ceramic raw powders are very small in size. With decreasing size particles tend to stick together due to the increasing surface to volume ratio. Homogenous and stable dispersions are a prerequisite for accurate measurements. Therefore a careful choice of the right dispersant, stabilizers (e.g. Sodium hexametaphosphate, SHMP), surfactants (e.g. IGEPAL® CA-630) as well as the application of ultrasound is paramount. Surfactants are amphiphilic molecules that support the dispersion of particles by reducing the surface tension between particles and the surrounding medium. Stabilizers, mostly polyionic salts, prevent agglomeration of particles by increasing electrostatic repulsion between the particles. Measurement conditions and input parameters are summarized for PSA liquid measurements in Table 1 and for Litesizer 500 analysis in Table 2. For the latter, the automatic settings for Measurement angle, Quality, Filter and Focus were selected.

Sample	Dispersion media	Ultra-sound	Stirrer speed	Pump speed	Meas. Time
$BaTiO_3$	4% SHMP in water	during meas.	Medium	Medium	30 s
NiO	water	during meas.	Fast	Medium	30 s
Al_2O_3	0.02% IGEPAL® in water	1 min before meas.	Fast	Fast	30 s

Table 1: Input parameters liquid measurements; Meas. = Measurement

Sample	Dispersion media	Cuvette	Temperature	Analysis model
TiO_2	Isopropanol	Quartz	25 °C	general
WC	Sunflower oil	Quartz	50 °C	narrow
Y_2O_3	water	Disposable	25 °C	general
Slip	water	Quartz	25 °C	general

Table 2: Input parameters Litesizer DLS-Experiments;

DLS settings vary with the sample to be measured. Dispersion media are optimized regarding perfect wetting and sample dispersion. Dense samples like WC (15.6 g/cm^3) that tend to sediment require viscous dispersion media such as sunflower oil to prevent sedimentation. By varying the temperature the viscosity of the medium can be optimized for the measurement. Cuvettes were selected according to the chemical properties of the dispersion media used. The hydrodynamic diameter was shifted to higher values in single measurements because of impurities of the sample. Therefore intensity weighted peak values were considered for determination of the mean particle size (diameter) for all measurements in order to provide meaningful statistics.

The stability of a slip colloidal suspension was determined by a zeta potential measurement using electrophoretic light scattering (ELS) technique in the Litesizer 500, according to conditions and parameters in Table 3.

Sample	Dispersion media	Cuvette	Temperature	Approximation
Slip	water	Univette	25 °C	Smoluchowski

Table 3: Input parameters Litesizer ELS-Experiments

The surface zeta potential of tubular ceramic membranes was determined with the SurPASS 3. A tubular ceramic membrane is composed of a porous ceramic support of cylindrical shape with a single or multiple channels (Figure 2). The inner surface in contact with the feed solution has an active ceramic layer which determines the porosity (cut off) of the membrane. This layer is characterized by pores of defined size for the retention of specific solutes in the feed.

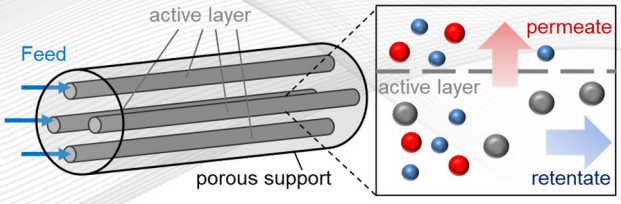

Figure 2: Scheme and functionality of tubular ceramic membranes

For zeta potential analysis of tubular membranes, samples of $Al_2O_3|Al_2O_3$ and $TiO_2|ZrO_2$ were cut to a length of 10 cm and mounted in a measurement cell developed for ceramic membranes (Figure 3). The streaming potential was generated by passing the aqueous 1 mmol/l KCl measuring solution through the porous ceramic support and the thin-film ceramic membrane. The pH of the aqueous KCl solution was adjusted automatically using the titration unit integrated in the SurPASS 3 instrument.

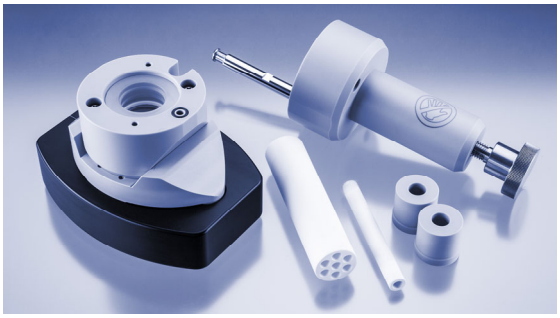

Figure 3: SurPASS 3 Measurement Cell for ceramic membranes with examples of single- and multichannel tubular ceramic membranes.

3 Results and Discussion

3.1 Ceramic raw powders - PSA measurements

Three different ceramic materials were characterized by their particle size distribution with the PSA series (Figure 4). $BaTiO_3$ is a ferroelectric ceramic material that exhibits piezoelectric properties. To reach a stable and homogeneous dispersion, SHMP was added and ultrasound was applied before and during the measurement. Barium titanate shows a broad but monomodal volume weighted particle size distribution with a main population in the size range between 0.2 µm and 2 µm.

In comparison Nickel oxide was analyzed. NiO is a metal oxide which is used in the ceramic industry to make frits, ferrites, and porcelain glazes. Its volume weighted particle size distribution is characterized by two populations, a minor one in the range of 1 µm and a prominent fraction between 3 µm and 20 µm.

Alumina - as the third material analyzed - shows properties of electrical insulation, high mechanical strength, low density and resistance to corrosion. It is one of the most cost effective and widely used materials in the family of high performance ceramics. In its powdered form it was dispersed in water containing 0.02% of the surfactant IGEPAL® CA-630.

The dispersion was further improved by sonication. Al_2O_3 shows a monomodal particle size distribution covering sizes between 1 µm - 10 µm. D-values of those three ceramic samples are summarized in Table 4.

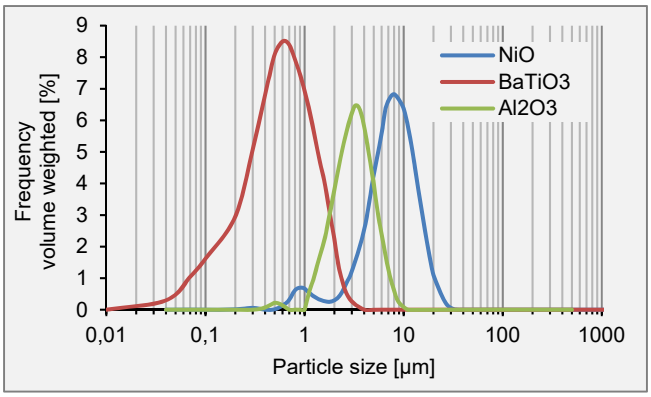

Figure 4: Volume weighted Particle size distribution of raw ceramic materials measured in liquid mode with the PSA series. Mie approximation was used for NiO and Al_2O_3 and Fraunhofer Approximation was used for $BaTiO_3$ to calculate particles size distributions. Mean values of three repetitions are illustrated.

Sample	D_{10} [µm]	D_{50} [µm]	D_{90} [µm]
NiO	3.05 ± 0.01	7.17 ± 0.03	13.8 ± 0.1
$BaTiO_3$	0.11 ± 0.01	0.48 ± 0.02	1.29 ± 0.01
Al_2O_3	1.60 ± 0.01	3.01 ± 0.01	5.25 ± 0.03

Table 4: D-values of ceramic materials measured with the PSA; mean ± SD

3.2 Ceramic raw powders - Litesizer measurements

The Litesizer 500 is able to measure small particles in the nm-range up to 10 µm. Particle size distributions of three independent ceramic samples were characterized (Figure 5). The first sample, TiO_2, is the most often used white pigment worldwide. Furthermore it is an electric insulator and sensitive to gaseous environment, hence it is present in oxygen sensors (2). TiO_2 powder was measured in isopropanol and displays a narrow monomodal intensity weighted particle size distribution with a mean particle size of 1.4 µm (Table 5).

Tungsten carbide (WC) was developed for cutting tools due to its extreme hardness and wear resistance. It is able to withstand high compressive stress and is resistant to oxidation even at high temperatures. The WC powder had to be measured in sunflower oil at 50 °C in order to prevent sedimentation of the dense powder. It shows a very narrow monomodal particle size distribution with a peak value at 187 nm (Figure 5).

Yttria (Y_2O_3) is characterized by hardness as well as chemical and thermal resistance. It is used to produce yttria stabilized zirconia (YSZ), solid-state lasers, and high temperature superconductors. It is host material for optical applications but also used in coatings or high temperature resistant materials. The measured monomodal particle size distribution shows a peak value at 567 nm (Figure 5).

The Polydispersity Index, as well as the mean particle size of the illustrated peaks are listed in Table 5.

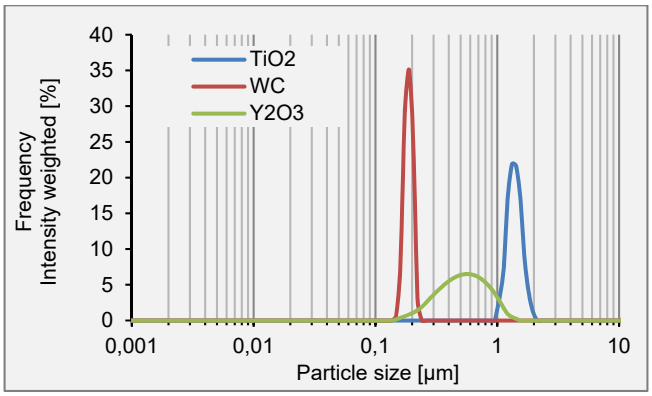

Figure 5: Intensity weighted particle size distribution of three ceramic materials, TiO_2, WC and Y_2O_3. Mean values of three measurements are displayed.

Sample	Mean particle size [µm]	Polydispersity Index [%]
TiO_2	1.40 ± 0.12	11 ± 14
WC	0.187 ± 0.005	16 ± 12
Y_2O_3	0.567 ± 0.008	24.6 ± 2.7

Table 5: Polydispersity Index, and mean particle size of the ceramic materials measured with the Litesizer 500; mean ± SD

3.3 Slip

A slip is a liquefied suspension or slurry of clay and/or other materials in water used in the production process of ceramic material (see Figure 1). To achieve optimal casting behavior a stable, well-dispersed colloidal suspension with an optimal particle size distribution is required.

To address this, a slip suspension was analyzed regarding particle size distribution and zeta potential with the Litesizer 500. The intensity weighted particle size distribution of a 1:1000 dilution in water pH 10 shows a monomodal function with a calculated mean peak position at 263 nm (Figure 6, Table 6).

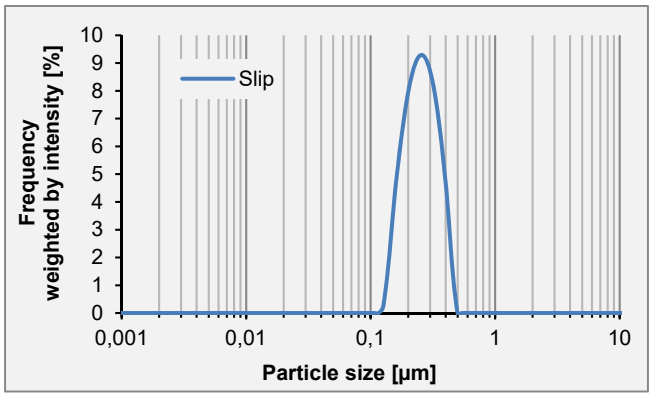

Figure 6: Intensity weighted Particle size distribution of Mean values of three measurements are illustrated.

Sample	Mean size [µm]	Polydispersity Index [%]
Slip	0.263 ± 0.002	18.9 ± 1.8

Table 6: Polydispersity Index and mean particle size of the slip sample measured with the Litesizer 500; mean ± SD

Figure 7 visualizes an exemplary zeta potential distribution of the slip suspension, with a mean zeta potential of -41.9 ± 0.6 mV.

A zeta potential of $\zeta < -30$ mV or $\zeta > +30$ mV indicates stable colloidal suspensions (3). The results suggest that the electrostatic repulsive forces between the slip particles are strong enough to prevent agglomeration and support an optimal casting behavior.

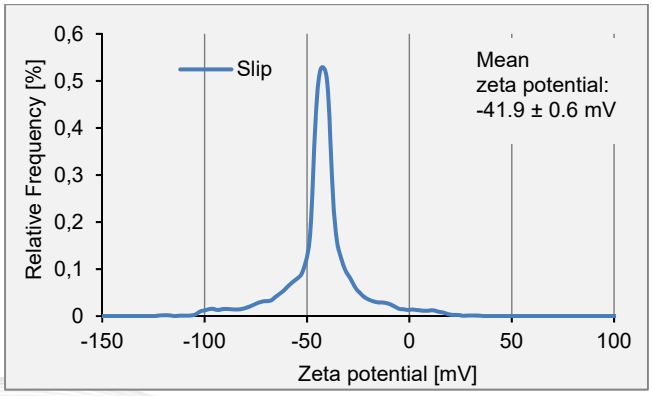

Figure 7: Exemplary zeta potential distribution of the slip sample.

3.4 Ceramic membranes – Zeta potential measurements on solid surfaces

Surface charge is the driving force for the retention in microfiltration, ultrafiltration, and nanofiltration processes and therefore directly linked to the membrane performance. Modifications in the surface cause new membrane properties that can be characterized with the SurPASS 3. Determining the Isoelectric Point (IEP), the pH of an aqueous solution at which the zeta potential reverses its sign, provides a strong indication for the chemical constitution of the solid surface.

Figure 8 shows the pH dependent change in the zeta potential of two tubular ceramic membranes used for microfiltration. A porous Al_2O_3 support coated with a microporous Al_2O_3 membrane layer (Al_2O_3 | Al_2O_3) was compared to a TiO_2 support coated with a microporous ZrO_2 membrane layer (TiO_2 | ZrO_2). The specific membrane properties are indicated by the position of the isoelectric point. The slightly acidic IEP (pH 4.3) of the TiO_2 | ZrO_2 membrane indicates a possible contribution of the porous TiO_2 support although the main information about the surface charge arises from the ZrO_2 microfiltration membrane.

The IEP of Al_2O_3 | Al_2O_3 is shifted to higher pH compared to TiO_2 | ZrO_2. For the Al_2O_3 | Al_2O_3 ceramic membrane the IEP was determined at pH 6.5 as a result of the microporous Al_2O_3 membrane layer on the porous Al_2O_3 support.

It can be assumed that in aqueous suspension metal oxide ceramic surfaces are covered with surface hydroxyl species, M-OH. At pH values above the IEP, the predominant surface species would be M-O^-, while at pH values below the IEP, M-OH_2^+ species predominate. The surface charges and with them also retention properties of the analyzed ceramic membrane differ dramatically between pH 4.3 and pH 6.5. While the surface of the TiO_2 | ZrO_2 membrane is negatively charged in this pH range, the Al_2O_3 | Al_2O_3 membrane surface is positively charged.

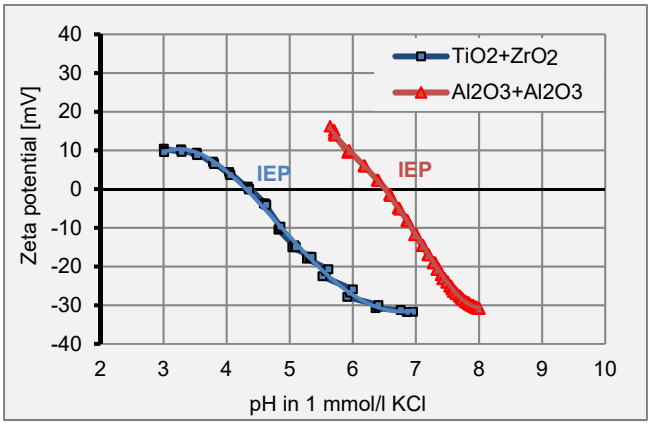

Figure 8: pH dependent zeta potential of two ceramic membranes, Al_2O_3 support coated with Al_2O_3 (Al_2O_3 | Al_2O_3) and TiO_2 support coated with ZrO_2 (TiO_2 | ZrO_2) measured in 1 mmol/l KCl.

4 Conclusion

Precise and accurate characterization of ceramic raw powders, slips as well as final ceramic products is a necessity and the base for high quality ceramic products. Particle size distribution and zeta potential are key parameters in ceramic product and process development as well as their quality control.

In this application report we outlined the use of laser diffraction and dynamic light scattering in the first ceramic processing steps, “powder processing” and “forming” (Figure 1), by determining particle size distributions. Furthermore two different techniques, electrophoretic light scattering and streaming potential measurements, were used to determine the zeta potential of powder dispersions such as slips in “forming” processes and solid surfaces of final ceramic products (Figure 1).

The PSA series offers the opportunity to determine particle sizes in a very broad size range up to 2.5 mm, to analyze uniform samples as well as complex sample types containing particles of different size classes or that tend to agglomerate. The reported measurements demonstrate that the PSA setup supports the use of stabilizers, surfactants, a variety of carrier liquids and sonication to improve the dispersion of particles, which is most critical in particle size analysis.

Ceramic raw powders are typically very small in size (< 5 µm) and supposed to be uniform. The Litesizer 500, using DLS technique, was capable to perform reliable and accurate particle size measurements within different carrier liquids and temperatures. In addition zeta potential measurements were performed successfully to estimate the stability of the slip suspension.

Finally, a dedicated measurement cell for single and multichannel ceramic membranes (4) was used to determine zeta potentials of solid surfaces with the SurPASS 3. The analysis revealed that sample specific and surface specific determination of the IEP by pH dependent zeta potential measurements provides indispensable information about existing surface properties or coating integrity and stability.

Notice: Supplementary analysis material available - please contact your local Anton Paar representative for more information.

5 References

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