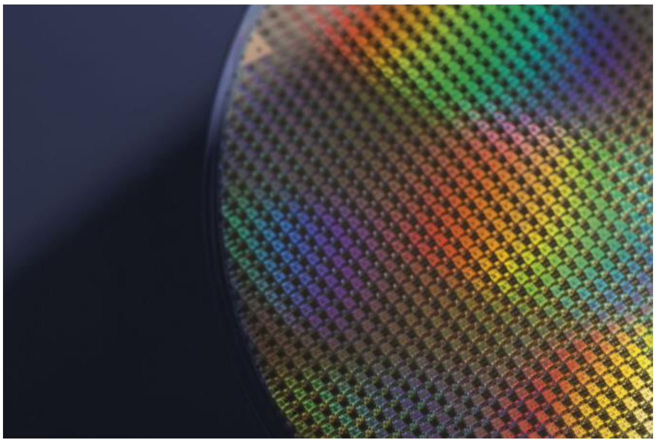
The Zeta Potential as an Indicator of Surface Properties

Relevant for: surface charge, solid surface, polymer, biomaterial, semiconductor

Whether in technological applications, biology or medicine, successfully developing new materials requires detailed knowledge of their surface properties. Surface chemistry often determines if a product is suitable for the intended application. An appropriate treatment is often necessary to tune the surface properties to fulfill the application requirements. However, the decreasing time available for such development processes demands a meaningful and rapid analysis of the solid surface, preferably close to the real conditions of the material application.



1 Introduction

Various physical methods are commonly used for a chemical analysis of the solid surface. However, these methods often require a time-consuming sample preparation, or they are not sensitive enough for the outermost surfaces. The zeta potential is a characteristic parameter for describing the surface chemistry of solids. It is located at the interface between a solid and a surrounding liquid. The zeta potential represents the surface charge, which occurs in the presence of an aqueous solution when reactive (functional) groups dissociate on hydrophilic surfaces or water ions adsorb onto hydrophobic surfaces. Varying the pH value of the aqueous phase influences the equilibrium between dissociation and adsorption processes, giving insights into the chemical behavior of the surface.

2 Surface Zeta Potential

The streaming potential and streaming current are measured to determine the zeta potential of macroscopic solid surfaces. An aqueous solution is set to flow across the solid surface under defined pressure conditions. The SurPASS™ 3 instrument by Anton Paar provides a comprehensive solution: With its range of different measuring cells SurPASS™ 3 determines the zeta potential of solids of various shape and size.

In the Cylindrical Cell, fibrous samples, powder or granules are arranged in a permeable layer. The measuring liquid streams through this fiber plug or powder bed (Figure 1). The differential pressure between both sides of the fiber or powder sample is determined by the sample packing density. This can be adjusted reproducibly using the monitored flow behavior.

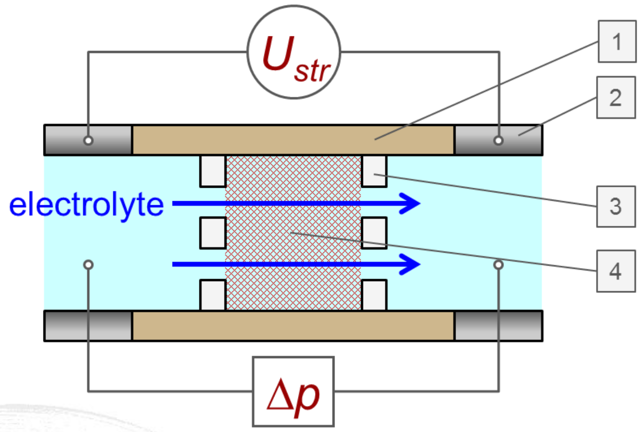


Figure 1: Schematic drawing of the Cylindrical Cell for fiber and powder samples (1 Cylindrical Cell, 2 electrode, 3 support disk, 4 sample plug)

In the measuring cells for samples with planar surfaces, i.e., the Clamping Cell and the Adjustable Gap Cell, a defined gap is set between two opposing sample surfaces. During the measurement the liquid flows through this gap and produces a pressure gradient and a charge separation at the solid/liquid interface. The streaming potential or streaming current is the electrical response to the shift in the surface charge.

In the Clamping Cell the height of the gap is defined by a spacer, whereas in the Adjustable Gap Cell the distance between samples is continuously adjusted (Figure 2). This allows investigations into the surface properties of samples with a rough surface, severe swelling behavior or a high degree of porosity.

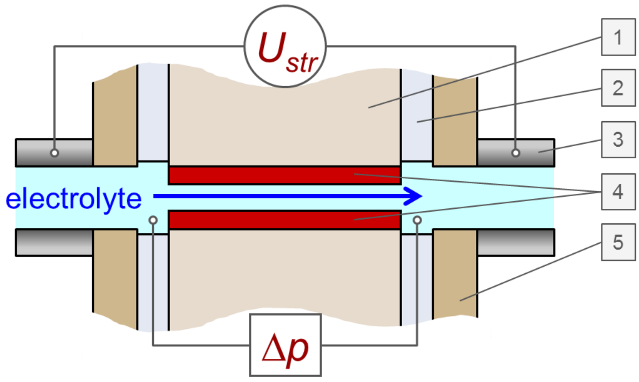


Figure 2: Schematic drawing of the Adjustable Gap Cell for planar samples (1 sample holder, 2 gasket, 3 electrode, 4 sample, 5 Adjustable Gap Cell)

Independent of the measuring cell used, the pressure difference is continuously decreased and the resulting streaming potential (or streaming current) is measured. The relationship between these two measuring parameters is linear (Figure 3), with the slope $dU_{str}/d\Delta p$ or $dI_{str}/d\Delta p$ being proportional to the zeta potential.

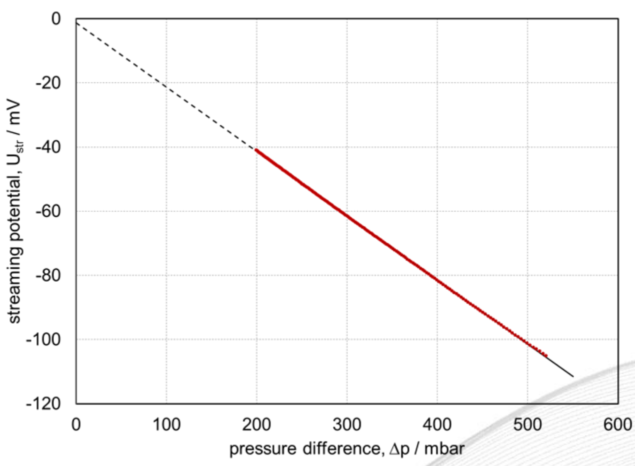


Figure 3: The zeta potential of a macroscopic solid surface is calculated from the slope of the linear dependence of streaming potential (or streaming current) on the differential pressure.

As a property of the interface between a solid and the surrounding liquid, the zeta potential is also influenced by the conductivity or electrolyte concentration of the liquid phase. A common electrolyte is an aqueous 0.001 mol/l solution of a simple salt such as KCl or NaCl. This allows a reproducible setting of the conductivity. The low electrolyte concentration also ensures a high sensitivity of the measuring method.

The preferred method for characterizing the solid surface is to vary the pH value of the aqueous solution and thus to carry out a titration of the surface. The dissociation of functional surface groups results in the formation of charge carriers on the surface. The number of these charge carriers changes with the pH value. This relationship allows qualitative insights into the chemistry of these functional groups. It is also possible to calculate the pK value of an acidic or basic surface entity. The integrated titration unit of SurPASS™ 3 automatically sets the pH value, e.g., to determine the isoelectric point.

The addition of chemicals to the aqueous solution (salts of multivalent ions, anionic or cationic surfactants, polyelectrolytes, proteins) gives further application-specific insights into the selective interactions of these components with the solid surface. For example, this allows investigation into the adsorption processes of surfactants on textile fibers or plastic surfaces. Another example is the change in the zeta potential of a filter membrane due to the selective adsorption of a divalent cation on its surface.

3 Applications

Applications for the streaming potential method are as numerous as the different sample geometries, which can be examined with SurPASS™ 3. A typical application is to qualify the effect of surface treatments.

Polymer surfaces typically show a low wettability and a poor adhesion for coating pigments or dyes. To improve these properties the polymer surface is subjected to pre-treatment (plasma treatment, flame treatment). The efficiency and durability of these procedures can be determined by the zeta potential. (1)

SurPASS™ 3 is also applicable in the manufacture of plastic parts. Traditional materials are successively replaced by composite materials, which combine an excellent mechanical strength with low weight. The reinforcing components in these composite materials are glass fibers or carbon fibers. Suitable modifications of their surfaces make these inorganic fibers compatible with the organic polymer matrix. The zeta potential is again a reliable parameter for characterizing the sizing of a glass fiber with a coupling agent, e.g., silanes (2).

Besides these inorganic fibers, it is also straightforward to characterize natural and synthetic textile fibers. The use of the zeta potential to analyze the cleaning procedures and dyeing processes for textiles has been described in detail in the literature (3), (4).

Advances in the development of filter membranes for drinking water and waste water treatment clearly show the benefits of the streaming potential method for analyzing membrane surfaces. Numerous reports describe the contribution made by this method to improve the understanding of the interaction between the membrane and salts or other substances dissolved in water (5).

In the development of biomaterials, knowledge of the zeta potential of the conventional metal and polymer surfaces used is of increasing importance (6), (7). For instance the medical application of an implant requires an appropriate surface treatment to accelerate protein adsorption and cell growth to ensure acceptance by the human body. Improving the hydrophilicity of the material surface is an essential step towards a high biocompatibility. The zeta potential supports such development. It is not only an indicator for a successful surface treatment but gives information about the functional groups, which are responsible for the change in the hydrophilic properties.

Last but not least, the streaming potential has been proven a useful method for the surface characterization of semiconductor substrates. An exemplary application is to evaluate the efficiency of cleaning processes and their effect on the surface chemistry (8). In the CMP process (Chemical Mechanical Polishing) the interaction of the CMP slurry (usually fine particles of alumina or silica) and the wafer surface to be cleaned is determined by the zeta potential of both slurry particles and the wafer itself. Knowledge of the zeta potential reduces the time for optimizing process conditions. The streaming potential helps to select an appropriate pH value or the type and minimal concentration of a surfactant.

4 Summary

The SurPASS™ 3 instrument provides a fully automatic and highly reproducible determination of the zeta potential of macroscopic solid surfaces. Besides the characterization of the surface chemistry of a variety of different solids, the prediction of their interaction with the environment is extremely helpful for a fast and successful development of products with new material properties.

Applications for SurPASS™ 3 range from the classical fields of polymers, technical fibers, textiles, and membranes to the investigation of biomaterials and semiconductor substrates. The examples in this report demonstrate the increasing importance of the zeta potential for the better understanding of material properties and process conditions.

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