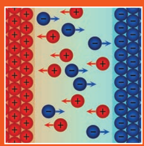
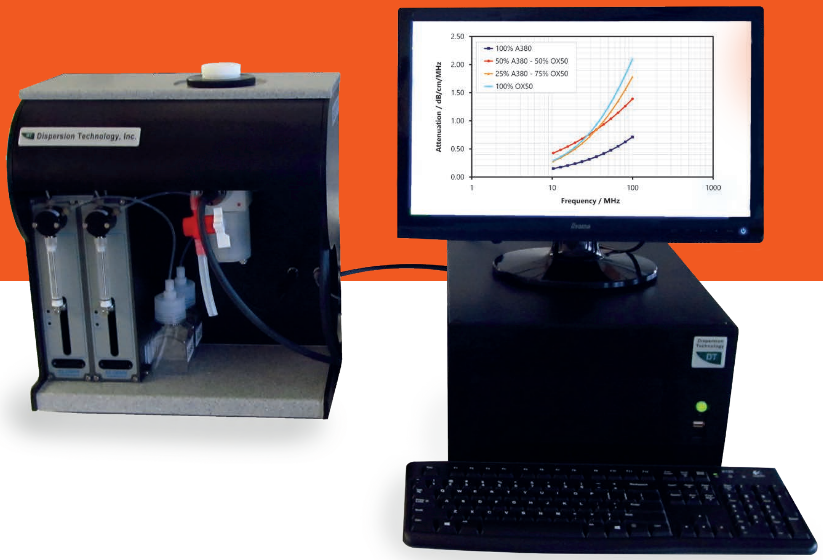
Use of acoustic methods and current flow measurement in battery research

Dr.-Ing. Christian Oetzel,
christian.oetzel@3P-instruments.com





Introduction

The development of rechargeable batteries (accumulators) with higher electrical power and service life as well as an increasing environmentally friendly production and disposal is one of the challenges of future technology. In addition, the manufacturing costs should be as low as possible in order to make end products, e.g. in the automotive sector, affordable for a wide range of customers.

With this goal in mind, there are different approaches in the research area, such as all-solid-state, lithium-air or lithium-sulphur batteries, all of which, however, are not yet ready for series production [1-3]. The most common system currently used in practice are the so-called lithium-ion NMC batteries (NMC: Nickel-Manganese-Cobalt). They are now used in key areas such as portable electronic devices (smartphones, tablets, notebooks) as well as in the entire electromobility sector (electric cars, hybrid vehicles, electric wheelchairs).

The manufacturing process of a modern accumulator is very complex and also includes numerous manufacturing steps in which organic solvents and generally liquid suspensions, i.e., hard material particles dispersed in a solvent, play an essential role. Particularly during processing, it is important that these systems are characterized in their original state with regard to properties such as particle size distribution, zeta potential or electrical conductivity in order to be able to assess the respective process step. It is precisely here that acoustic methods are available which in contrast to conventional optical methods such as static light scattering dynamic image analysis or electrophoresis can also be used in more concentrated dispersions [4].

In this article, the mentioned measurement methods are first briefly summarized. Subsequently, the functionality of an NMC battery cell is discussed, in order to discuss afterwards the areas of application of the methods in the production of such an accumulator.

Principle of measurement of acoustic methods and frequency-dependent current flow measurement – an overview

The methods "acoustic attenuation spectroscopy" for particle size determination and "electroacoustics" for determining zeta potential are predestined for many areas of application in battery development: Their great advantage is the possibility of measuring dispersions in their original state, i.e. without dilution or special preparation. Details on both methods can be found e.g. in [4-5] and a short summary is given below.

Acoustic attenuation spectroscopy for particle size measurement

The principle of acoustic attenuation spectroscopy for size measurement is shown in Fig. 1: A sound transducer transforms a high-frequency signal into an ultrasound wave. It is a short-wave package with a very constant amplitude and wavelength that will be launched into the dispersion to be characterized. To avoid overlap-effects, every individual "burst" is shorter than the time of transmission. During transmittance of the wave through the dispersion, it will be attenuated due to different loss interactions with the particles dispersed in the system [4-5].

The attenuated signal is detected by the sound receiving transducer and forwarded to the computer for signal-conditioning and analysis. Apart from the specific effects in the dispersion (I_0 to I), the attenuation is dependent on the gap L between sender and detector as well as on the soundwave frequency f:

$$\text{attenuation}\left[\frac{\frac{\text{dB}}{\text{cm}}}{\text{MHz}}\right] = \frac{10}{f[\text{MHz}]L[\text{cm}]}\log\frac{I_{in}}{I_{out}}[\text{dB}] \quad (1)$$

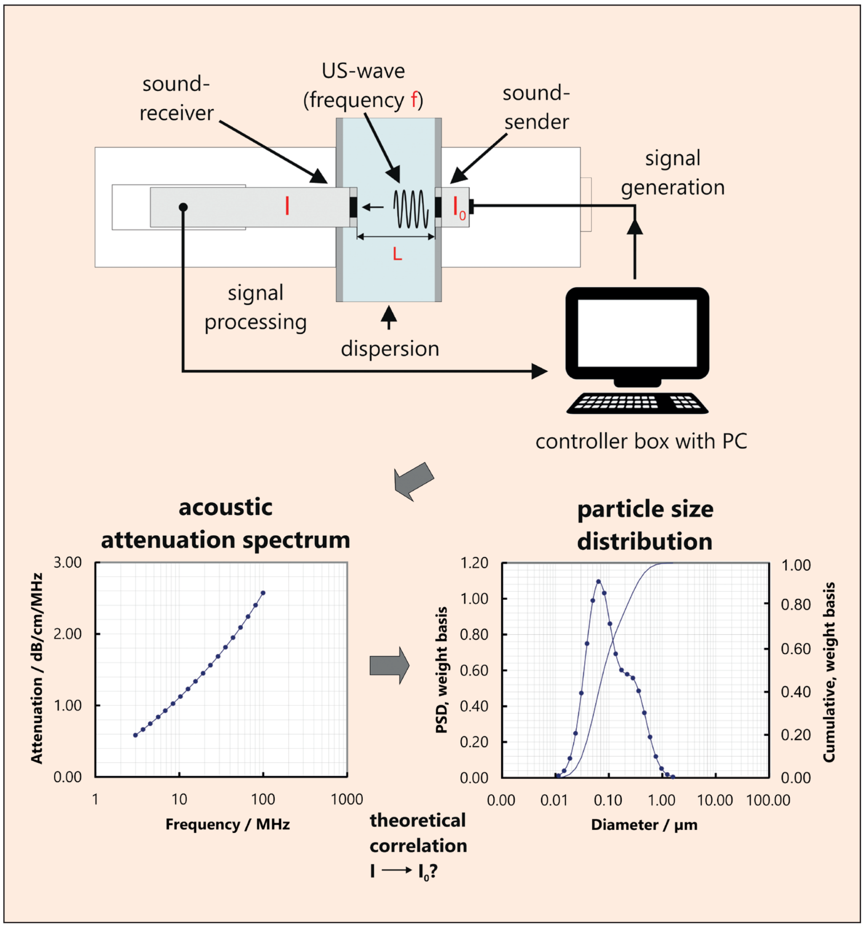


Figure 1 *Measurement principle of acoustic attenuation for particle size measurement*

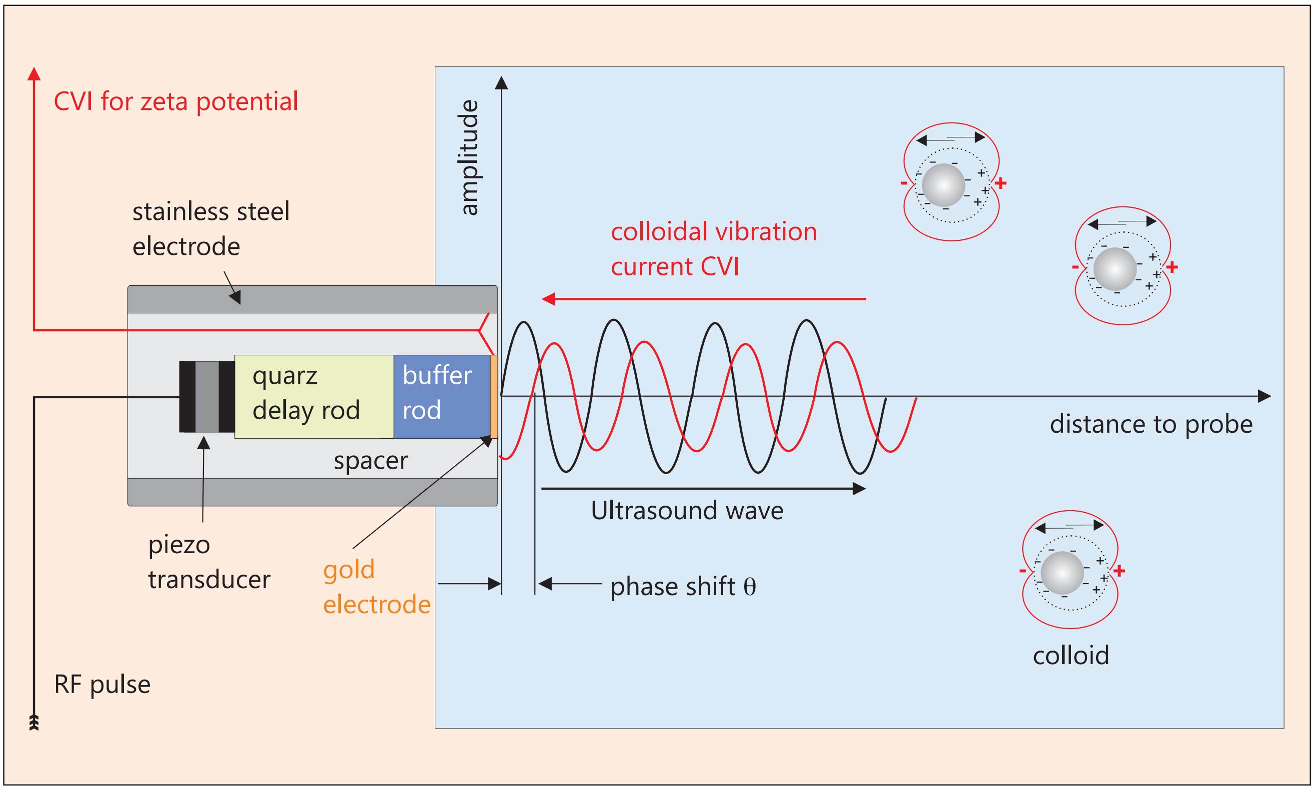


Figure 2 *Measurement principle of electroacoustic for zeta potential measurement*

The acoustic spectrometers from Dispersion Technology (DT) are using this method for particle sizing: The frequency range is 1 to 100 MHz and, due to the variable gap, a concentration range of 0.1 to 60 vol.-% can be realized. The measured spectrum will be fitted on the bases of the different theories describing the material specific attenuation mechanism [4-5].

Electroacoustic for zeta potential determination

A comprehensive description of this method for determining zeta potential can be found in [4-5]. Fig. 2 shows the measuring principle schematically.

A high frequency signal (RF-pulse) is transferred into an ultrasound wave by means of a piezo transducer. This wave passes a quartz delay rod for internal calibration, then a buffer rod and enters the dispersion as a short pulse with a narrow frequency distribution. The colloidal particles in the dispersion start a frequent motion relative to the surrounding liquid because of their mass inertia. Thus, the particles are shifted relative to their diffuse double layer: an oscillating electric field is generated which induces a measurable, alternating current – the colloidal vibration current (CVI). This is measured as a potential between two electrodes and can be used to determine the colloidal properties of the sample. The two important measurement parameters are the magnitude of the CVI signal which determines the absolute amount of the zeta potential and the phase shift θ between the ultrasound wave and CVI signal which determines the sign. The relation between the CVI and the zeta potential of the particles in the suspension in aqueous systems is normally described using the SDEL-theory [4]:

$$\mu_d = \frac{\varepsilon_m \varepsilon_0 K_S}{\eta K_m} \frac{(\rho_p - \rho_s)\rho_m}{(\rho_p - \rho_m)\rho_s} \qquad (2)$$

Advanced theories for polar and non-polar systems are summarized in [6]. As with the acoustic attenuation method for size, the concentration range is 0.1 to 60 vol.-%. Furthermore, the system can be used for pumping or stirring systems and thus even for sedimenting particles.

All electroacoustic systems from DT are using this technique for zeta potential measurement.

Measurement of the electric conductivity in weak and non-polar organic solvents

A special measurement setup consisting of two coaxial stainless-steel electrodes and a guard electrode was used. The task of the latter is to eliminate leakage currents between the measuring electrodes. During a measurement, the instrument applies a sinusoidal voltage to the outer electrode and measures the current that flows through the sample to the inner electrode. The frequency of this applied voltage is changed depending on the measured conductivity in the range from 1 to 10 Hz.

The method is implemented in the DT-700 and a measurement range of 10^{-4}-10^{-11} S/m can be realized.

Functional principle of an NMC battery cell

The setup and the functional principle of an NMC battery cell is shown in Fig. 3.

The anode (-) consists of an 8-18 µm thick copper foil coated with active material (graphite). The cathode (+) is a 15-25 µm thick aluminum foil coated with NMC active material. A microporous separator, which consists of a microporous polymer film normally coated with Al_2O_3, AlOOH or SiO_2, separates the two electrodes from one another. The whole system is immersed in an electrolyte liquid.

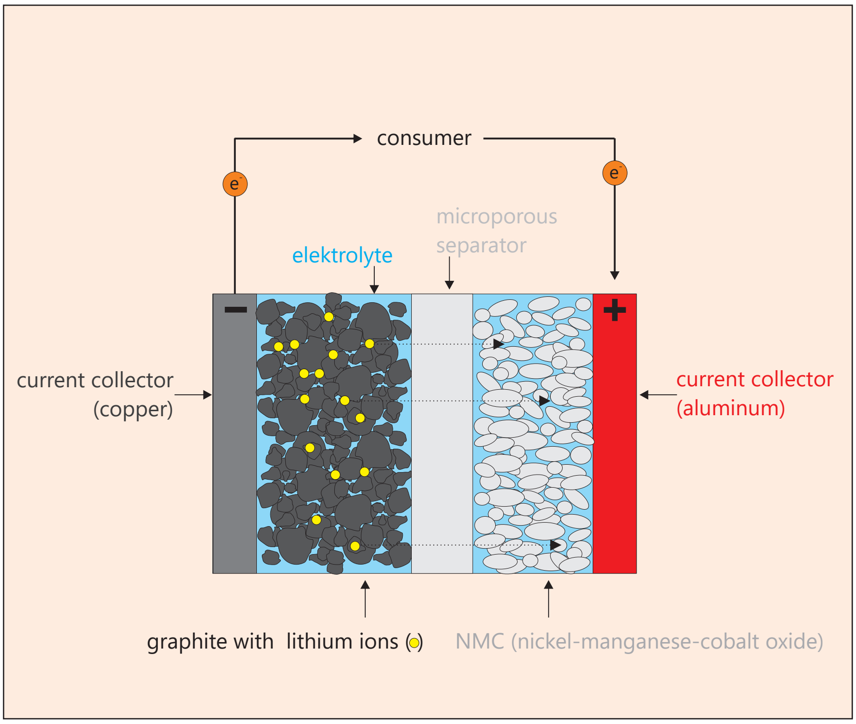


Figure 3 *Setup and working principle of a NMR accumulator*

During the discharge process, a current of electrons flows through the consumer. At the same time, positively charged lithium ions that are stored in the active material of the anode move through the separator to the cathode and are stored there in the NMC layer (charge equalization). During the charging process, the accumulator is connected to a power source and the process is reversed.

Suitable electrode-active materials for the Li-ion transfer as well as a good electrode wetting of the active materials are decisive for an optimal functionality. In addition, the ceramic coating ensures that the separator can be laminated and is thermally stable.

Suspensions and organic solvents play an essential role in the production of the cathode starting material NMC and the production of electrolytes. Furthermore, the coating process of the separator and the anode and cathode production are each carried out via a suspension route.

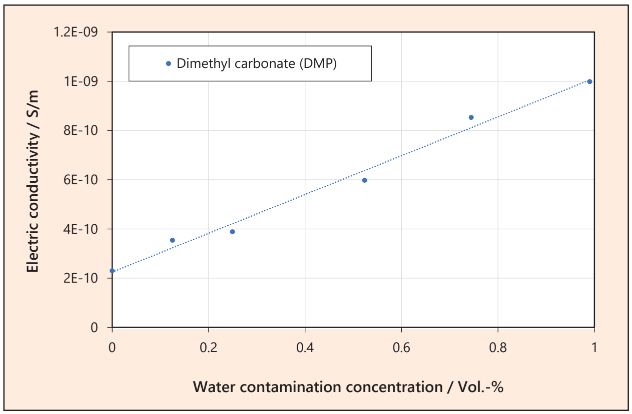


Figure 4 Electric conductivity in dependence of water contamination concentration, measured by means of a DT-700

Possible uses of acoustic methods and electric conductivity measurement for the manufacturing of NMC batteries

The main application of the acoustic methods is in the field of separator production as well as cathode and anode manufacturing, conductivity measurements are particularly useful for electrolyte production and cathode production.

Manufacturing of the liquid electrolyte

The electrolyte of the NMC battery cell consists of a conductive salt and an organic solvent or solvent mixture. In addition, certain additives that improve the long-term stability of the unit are used. Lithium hexafluorophosphate ($LiPF_6$) is used as the conductive salt, possible solvents include dimethyl carbonate (DMC) or ethylene carbonate (EC). Vinylene carbonate (VC), for example, is used as an additive. All components are mixed together in a reactor.

It is necessary that the liquid electrolyte is as free of water as possible, as this results in a decomposition reaction of the conductive salt. Fig. 4 shows an example of electric conductivity measurements on a pure DMC solvent in dependence of water contamination concentration.

Even small amounts of water-contamination lead to an increase in electric conductivity, measured using the DT-700. Thus, this method/parameter is ideal for checking the quality of the liquid electrolyte.

Manufacturing of the separator

The separator consists of a porous polymer membrane which is usually produced by a wet chemical melting process from a polymer-additive mixture using temperature, pressure and a subsequent rolling process step.

To increase the thermal stability in high-temperature applications, separators are coated with ceramic particles (e.g. Al_2O_3, AlOOH, SiO_2) in a subsequent step: This is done using a suitable suspension and a gravure roller. The decisive process parameters for the coating process include the particle size distribution of the ceramic particles in the suspension and their stability against agglomeration. At this point, the acoustic methods "acoustic attenuation spectroscopy" (particle size distribution) and "electroacoustic" (zeta potential measurement) are particularly suitable because, in contrast to optical methods, the suspension can be measured in its original state, i.e., without dilution or other preparation steps.

For coating with Al_2O_3 particles e.g. aqueous suspensions are used. The maximum agglomerate size should be around 2-3 µm. Fig. 5 shows the dependence of the particle size of such an alumina suspension (12 wt.-% Al_2O_3 in water) on the pH value, in Fig. 6 the associated zeta potential vs pH measurement curve can be seen. Obviously, due to the high zeta potential, the suspension shows a monomodal size distribution with maximum diameters of about 1 µm in the weak acidic range (pH = 5), whereas in the weak basic range (pH = 9) with a zeta potential close to 0 a clear tendency towards agglomeration can be seen (agglomerate diameter up to 10 µm).

Thus, the pH should be set < pH 7 for a good working coating process with this type of suspension or, alternatively, suitable stabilizers should be used.

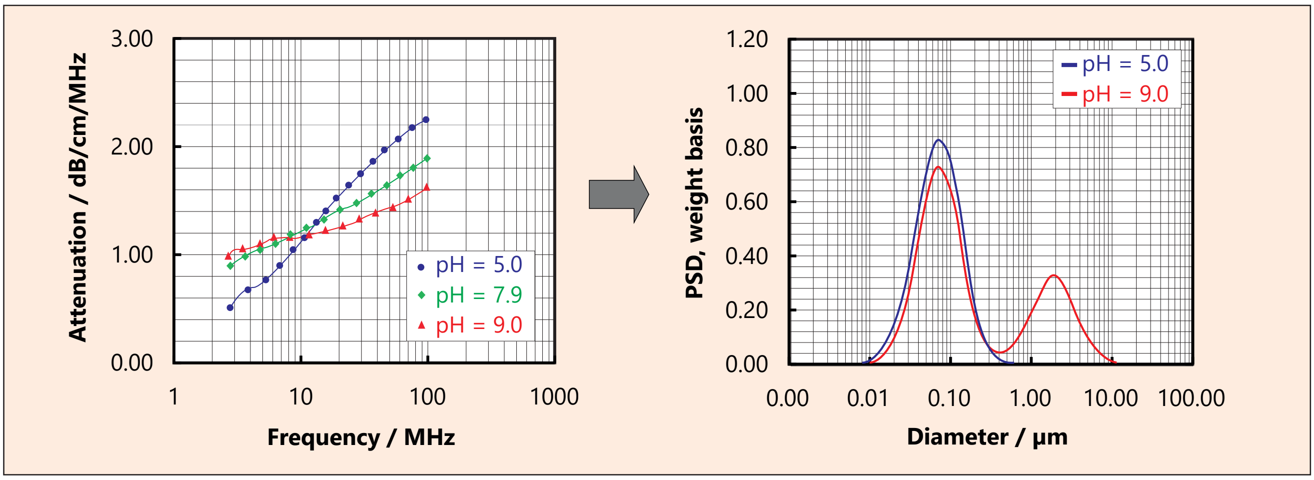


Figure 5 Particle size distribution of an aqueous, 12 wt.-% Al_2O_3 suspension in dependence of pH (measured using a DT-1202)

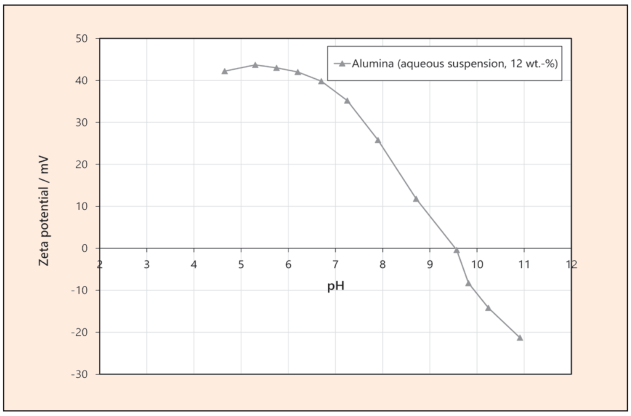


Figure 6 *Zeta potential vs. pH of the 12 wt.-% Al_2O_3 suspension in Fig. 5 (measured with DT-1202)*

Electrode production

Both the anode and cathode manufacturing of a lithium-ion NMC battery works suspension-based by coating the electrode material (copper or aluminum foil) using special application tool (e.g. lot nozzle or anilox roller).

At the cathode, the aluminum foil is coated with a $Li(NiMnCo)O_2$-in-NMP-suspension (N-methyl-2-pyrrolidone), which also contains carbon black and a binder (PVDF). An aqueous graphite-carbon black suspension is used for the anode (copper foil), which also contains a binder (carboxymethyl cellulose, CMC) and an additive (styrene-butadiene rubber, SBR). In this process step, the suspension properties of course will influence the quality of the coated electrodes, such as layer thickness accuracy or adhesion between substrate and layer.

The following example shows the possibilities of acoustic attenuation spectroscopy (particle size measurement) for electrode production: An aqueous, approximately 30 wt.-% graphite-carbon black CMC paste was measured with the aid of a DT-1202 regarding particle size distribution. The carbon black had a mean particle size of about 400 nm, the graphite of about 3.8 µm. Fig. 7 shows the measured attenuation spectrum and particle size distribution of the final produced paste.

For the calculation the Rouse-Bueche-Zimm model for structural losses was take into account [4].

Conclusion

In this article, the possible uses of the three methods "acoustic attenuation spectroscopy for particle size", "electroacoustic for zeta potential" and "electric current measurement for electric conductivity in organic solvents" for NMR battery production process were investigated.

The acoustic methods are in particular ideal to characterize the suspensions used for electrode manufacturing and separator coating due to their possibility to measure in original concentrated systems.

The electric current measurement on the other hand is predestined to check the liquid electrolyte regarding water contamination. Thus, all systems can play an important role both in cell development and later in quality checks during battery production.

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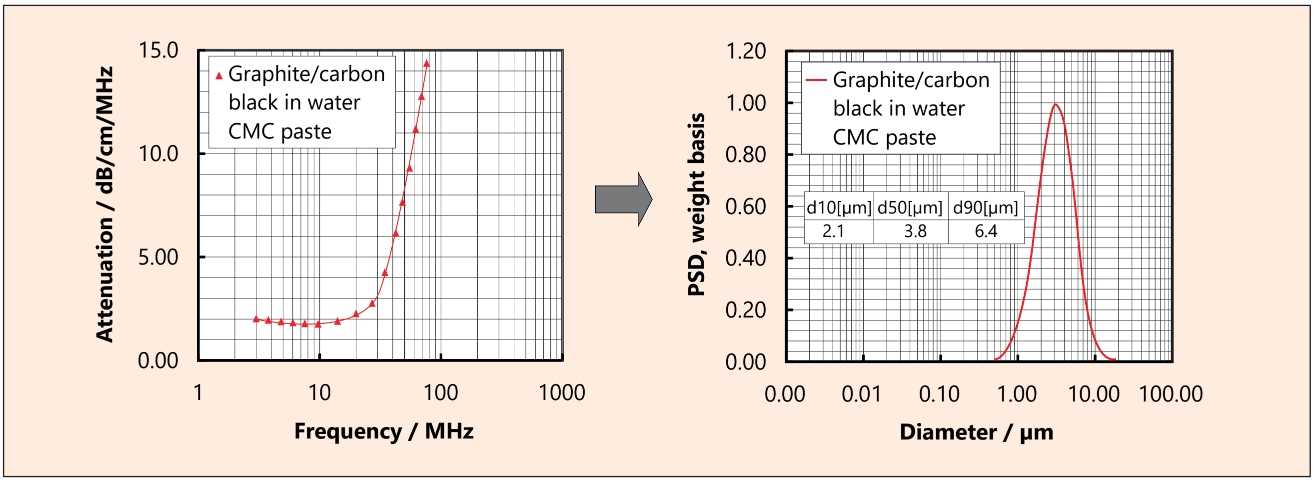

Figure 7 *Particle size distribution of an aqueous, 30 wt.-% graphite-carbon black-CMC paste (measured by means of the DT-1202)*