APPNOTE 6-01

Use of acoustic methods in battery research

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Characterization of particles · powders · pores

Introduction

The development of rechargeable batteries (accumulators) with higher electrical power and service life as well as more environmentally friendly production and disposal is one of the challenges of future technology. In addition, the reduction of manufacturing costs is a critical factor 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 in use are the so-called lithium-ion NMC batteries (NMC: Nickel-Manganese-Cobalt). They are used in key areas such as portable electronic devices (smartphones, tablets, notebooks) as well as in the entire e-mobility 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 dispersions are characterized in their original state with regard to their dispersion state (degree of agglomeration) and electrochemical properties like zeta potential or electrical conductivity. Only then the production process can be understood fully and also kept stable. In addition, it is important for the further development and improvement of battery cells, for example, to substitute environmentally problematic components such as the NMP currently frequently used for electrode production and to investigate alternatives with regard to the coating process.

A comprehensive characterization of the original liquid systems used in the process and the dispersion state of the particles is possible with the acoustic spectrometer DT-1202 (https://www.3p-instruments.com/analyzers/dt-1202/) in combination with the conductivity measurement system DT-700 (https://www.3p-instruments.com/analyzers/dt-700/). This will be demonstrated below using various example measurements from the field of lithium-ion battery development and quality control.

Fields of application of the DT-1202 using the example of an NMC battery production

The DT-1202 (Fig. 1) is a modern acoustic spectrometer that combines acoustic attenuation for size measurement and electroacoustics to determine the zeta potential of dispersions in original concentration. In combination with the DT-700 (electric conductivity probe for organic solvents), even highly non-polar systems can be analyzed in detail.

Figure 1 *DT-1202 (left): Combination of acoustic attenuation for particle size distribution, electroacoustics for zeta potential and electric conductivity for aqueous systems; DT-700 (right): Electric conductivity of organic systems*

A comprehensive description of both acoustic methods can be found in [4]. The most important features and benefits of the system are summarized here:

- Particle size, zeta potential, electrical conductivity of dispersions in the concentration range of 0.1 - 60 vol.-%, size range of 1 nm to 100 µm and conductivity range of 10^{-1} to 10 S/m
- Great flexibility in terms of application: Sample can be stable or sediment, thin liquid or paste-like, aqueous or organic, highly or slightly conductive
- Works according to ISO 20998-1 (acoustic attenuation, particle size) and ISO 13099 (electroacoustics, zeta potential)

The functional principle of a NMC battery cell is shown in figure 2, the working principle of the cell can be found, for example, in [5].

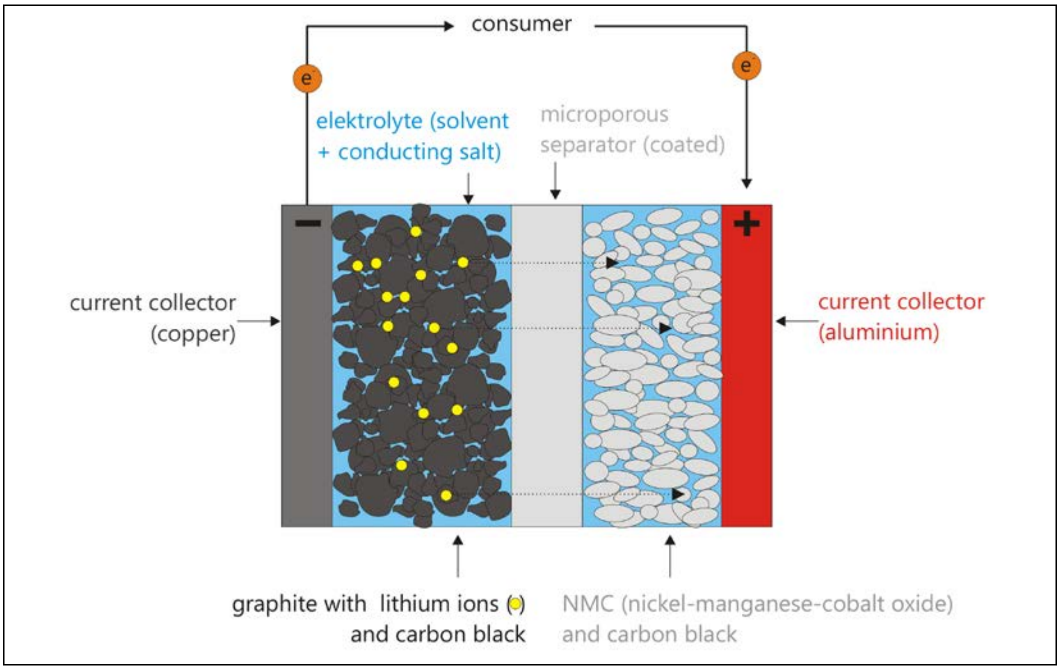

Figure 2 *Setup and functional principle of a NMC accumulator*

The main field of application for acoustics is certainly the manufacturing process of the active electrode materials, the optimization of the suspension production and its characterization and the subsequent coating process of the collectors (electrode production). In addition, the focus is on the production of the separator and the electrolyte.

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).

Usually the slurry used for cathode production consists of the active material NMC ($Li(NiMnCo)O_2$), dispersed in the solvent NMP (*N*-methyl-2-pyrrolidone), a proportion of conductive carbon black and a binder (e.g. Polyvinylidene fluoride, PVDF). The binder has the task of stabilizing the subsequent layer and ensuring good adhesion to

the electrode foil. NMP is used as a dispersing medium for the cathode suspension due to its high polarity and good thermal stability, but is controversial in terms of safety and health.
The suspension for the anode can be an aqueous system with graphite and carbon black dispersed in it, also a binder (e.g. carboxymethyl cellulose, CMC) with the same task as PVDF for the cathode slurry and some additives for stabilization.
For cathode and anode manufacturing, the suspension properties will influence the quality of the coated electrodes, such as layer thickness accuracy or adhesion between substrate and layer. The following example of the characterization of an approximately 30 wt.-% aqueous graphite/conductive carbon black/binder suspension using the small volume size cell (SVC) of the DT-1202 shows the possibilities of acoustics for improving electrode production.

Figure 3 shows the acoustic attenuation spectrum and calculated particle size distribution of the paste, measured in its originally state. Changes in the mixing ratios of the components and the dispersion conditions can be analyzed directly with this technique with regard to their influence on the degree of agglomeration of the finished paste.

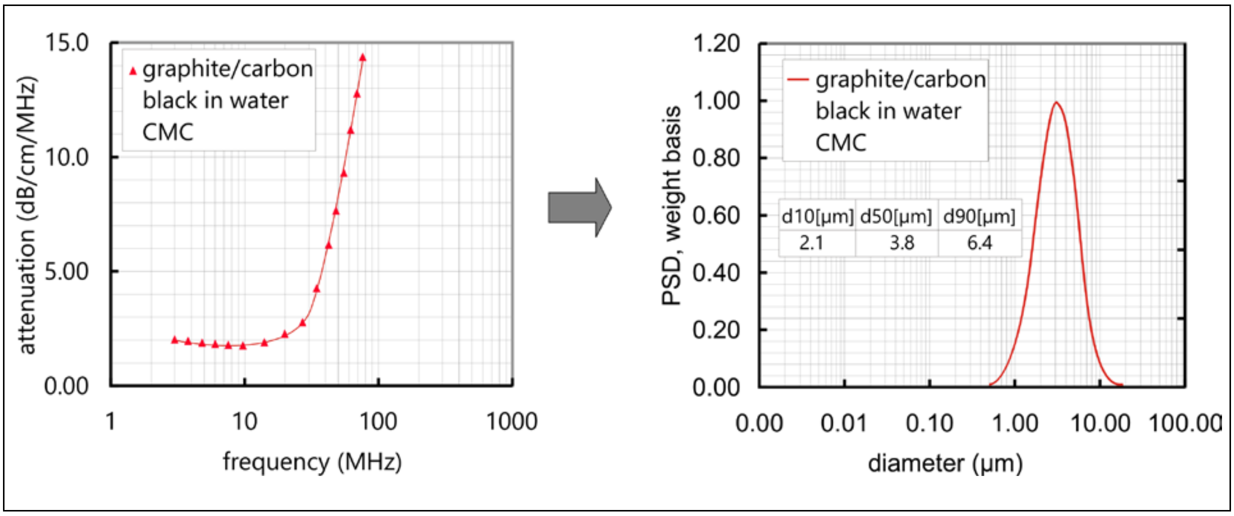

Figure 3 *Particle size distribution of an aqueous, 30 wt.-% graphite carbon black-CMC paste (measured by means of acoustic attenuation spectroscopy, DT-1202)*

Figure 4 shows the dependence of the zeta potential of the dispersed particles - measured by means of electroacoustics - and the electrical conductivity of the suspension as a function of the pH value, the initial pH was 12.75 with a zeta potential of -18.4 mV and an electric conductivity of 0.81 S/m. The titrants used were 1 molar NaOH and HCl. These two electrochemical parameters directly influence the agglomeration state and rheological properties of the slurry and thus the quality of the produced layer. It tends to be helpful for the coating process to maximize the absolute value of the zeta potential while keeping electrical conductivity as low as possible. A processing range of around pH 8-13 is therefore recommended for this slurry.

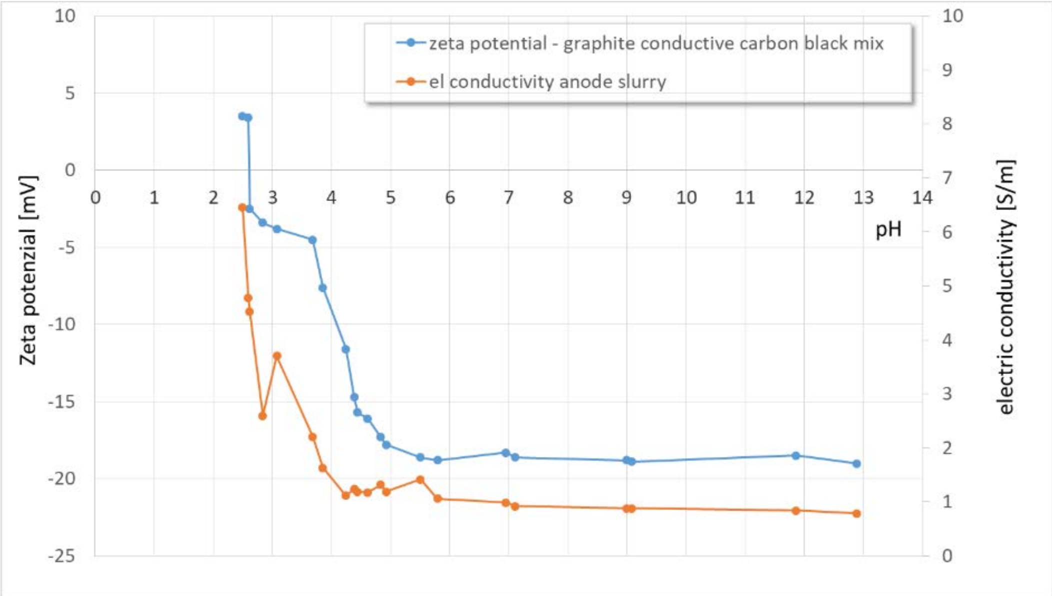

Figure 4 *Zeta potential and electrical conductivity vs. pH of the 30 wt.-%t aqueous graphite/conductive carbon black/binder suspension, measured with DT-1202*

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 "electroacoustics" (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 and correspondingly large repulsive forces to prevent agglomeration, 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 alkaline 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 to pH < 7 for a well working coating process with this type of suspension or, alternatively, suitable stabilizers should be used.

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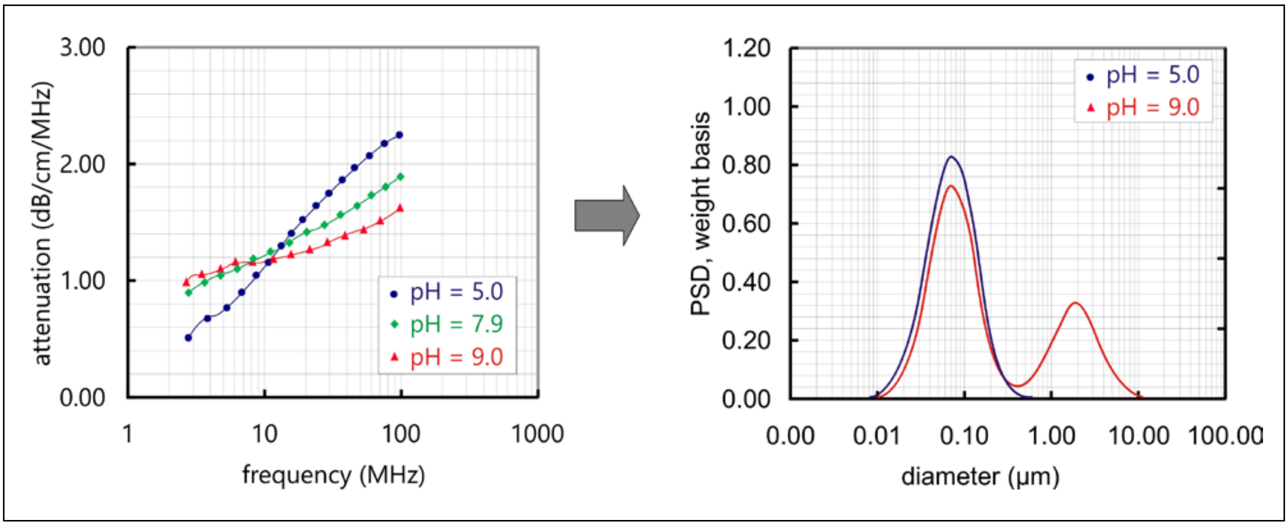

Figure 5 *Particle size distribution of an aqueous, 12 wt.-% Al_2O_3 suspension in dependence of pH*

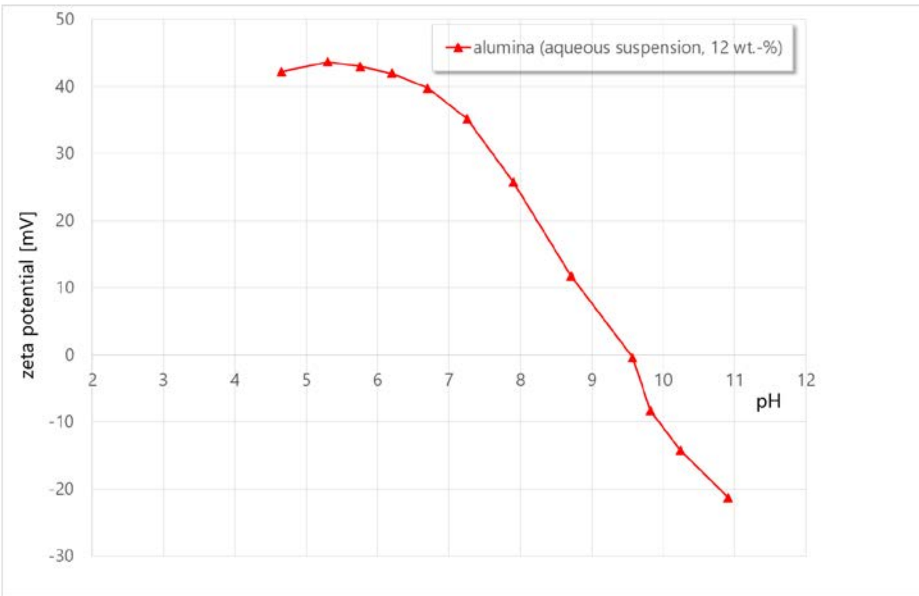

Figure 6 *Zeta potential vs. pH of the 12 wt.-% Al_2O_3 suspension in Fig. 5*

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 causes a decomposition reaction of the conductive salt.

Fig. 7 shows an example of electric conductivity measurements on a pure DMC solvent in dependence of water contamination concentration, measured using a DT-700.

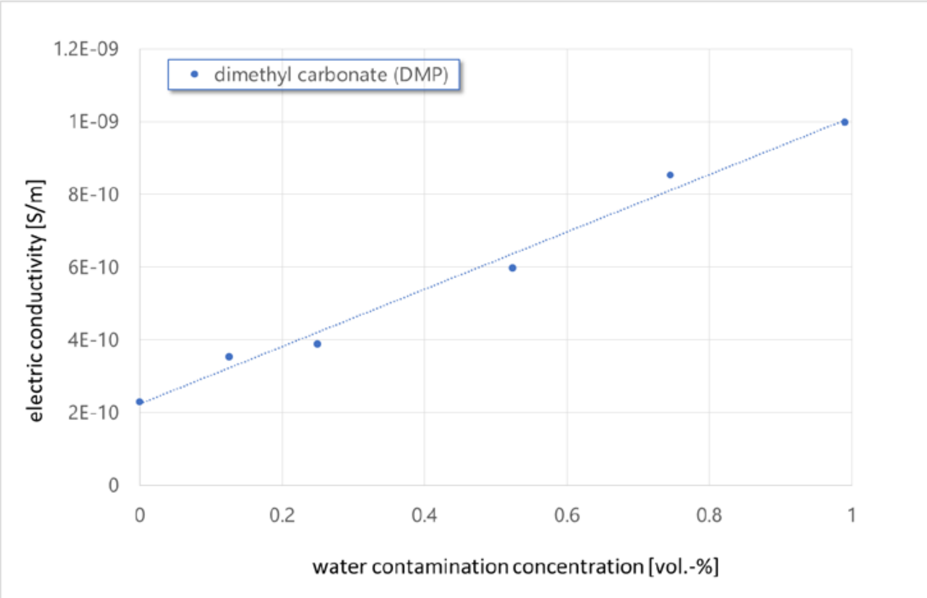

Figure 7 *Electric conductivity in dependence of water contamination, measured by means of DT-700*

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.

Conclusion

In this article, the possible uses of the three methods “acoustic attenuation spectroscopy for particle size”, “electroacoustics for zeta potential” and “electric current measurement for electric conductivity in organic solvents” for NMC battery production process were investigated. The acoustic methods in particular are ideal to characterize the suspensions used for electrode manufacturing and separator coating due to the 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.

References

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