MAGNETIC RESONANCE FOR BATTERIES RESEARCH AND MANUFACTURING

Analyzing electrode slurries to optimize cost of lithium-ion battery production using the Bruker minispec

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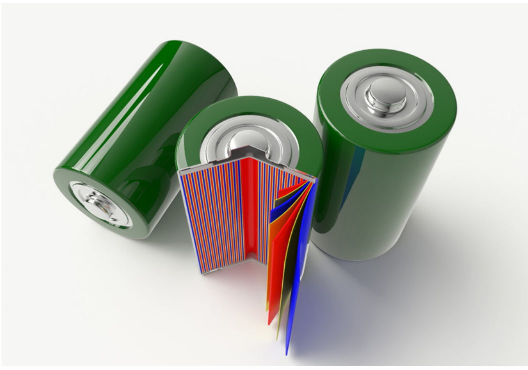
Innovation with Integrity

Introduction



There is a growing demand for new manufacturing of Lithium-ion batteries (LIBs) that have improved charge lifetimes, energy densities, charge-discharge rates, and safety all while coming at a lower cost. Such improvements are critical as the demand for electric vehicles, large scale stationary power storage systems and consumer electronics continues to grow. The major contributor to a battery's cost structure is materials and material waste in the production process. Refining methods for the coating process of the electrodes allows the manufacturer to minimize input and waste of expensive material. One of the fundamental steps in improving the performance of LIB's is optimizing the process for coating the electrodes with electro-chemically active materials. It is important that the coating material is applied to the electrode in an evenly distributed manner. The viscosity and particle distribution of the coating precursor must be optimized to provide the most efficient manufacturing and performance properties for the final battery. The coating precursor is an aqueous suspension and often referred to as slurry. Here we describe how the Bruker minispec Time Domain NMR (TD-NMR) spectrometer can measure critical physical properties of a slurry and allows manufacturers to optimize the coating process for lithium-ion batteries.

Electrode slurries are highly viscous water-based suspensions that contain a large amount of solid fraction. This solid fraction is often made up of a combination of carbon-based conducting material and a polymeric binder. The slurry material is applied as a coating to the battery's anode current collector material which is typically copper. The chemical formulation of slurries is optimized for electro-chemical conductivity. However, the rheological properties of these suspensions will directly affect their processing behavior [1,2]: from mixing (homogenization), to processing until application for high and uniform coating performances. It is essential for the battery cell manufacturing process to define the optimum viscosity of the slurry to match processing behavior and material stability.

The time stability of slurries as a suspension is of great interest for manufacturers and it can be linked with the time scale in which sedimentation effects start separating heavy and light fractions into distinct phases [3]. Here, viscosity and density play a major role affecting not only sedimentation rates and coating performance, but also the processing efforts and the continuous mixing of slurries to keep the material at high homogeneity levels. As most of the cost of a battery is linked to materials, reducing raw material input and waste significantly reduces the overall price point of the finished battery.

Highly viscous slurries are expected to be more stable against sedimentation effects, whereas its ease of handling and coating performance can be negatively impacted by high densities [1]. Low-viscosity slurries are easier to handle, exhibit better coating performance, but are more susceptible to sedimentation effects. Monitoring stability and understanding physical properties of slurries is essential to achieving high-quality, consistent, and cost-effective battery cell production.

Monitoring slurry stability against sedimentation using the Bruker minispec

^{1}H relaxation measurements of solvents in slurries are directly affected by both the concentration of solid particles in the suspension and the homogeneity of the mixture. The higher the concentration of solid particles versus solvent, the faster the measured relaxation profile will be due to interactions between solvent molecules and solid surfaces of particles.

For slurries in a homogeneously mixed state, solid particles are found to be evenly distributed through the solvent and surface relaxation effects are experienced and averaged throughout solvent molecules. When at rest, sedimentation effects in slurries will induce the separation of a lower viscosity phase with low concentration of particles, and a high viscosity phase accumulating a large concentration of solid fraction. As a result of this separation, the effects of surface-induced relaxation are now very distinct in those two phases.

The Bruker minispec brings a fast and robust method for non-invasive monitoring and early identification of sedimentation in slurry samples, as well as the quantification of high- and low-viscosity separated phases versus time. Temperature-controlled slurry stability measurements are carried out within about 1 minute total data acquisition time. The sample requires no additions or any preparation allowing for measurements in the original, unchanged state. The only pre-measurement treatment is a tempering step assuring the exact same temperature of the sample and the NMR system. With a single sample, stability measurements can be set to run periodically, providing a detailed report over a user-defined time scale.

The time-dependent increase of a high-mobility phase in the sample is directly linked to separation processes. Different slurry formulations and additive compositions can be used to design key physical properties like de-mixing behavior over time. 3 significantly different formulations have been investigated in this case-study whereas Slurry 1 significantly showed a stability-optimized formulation (see Figure 1, left). The change dynamics of the sample at any given time can be described as a de-mixing rate. These rates are, of course, not constant for different formulations, but interestingly, they are also not necessarily constant over time for a given formulation (see Figure 1, right). Especially Slurry 2, which has a strong tendency towards separation, shows a rather low rate of de-mixing shortly after preparation.

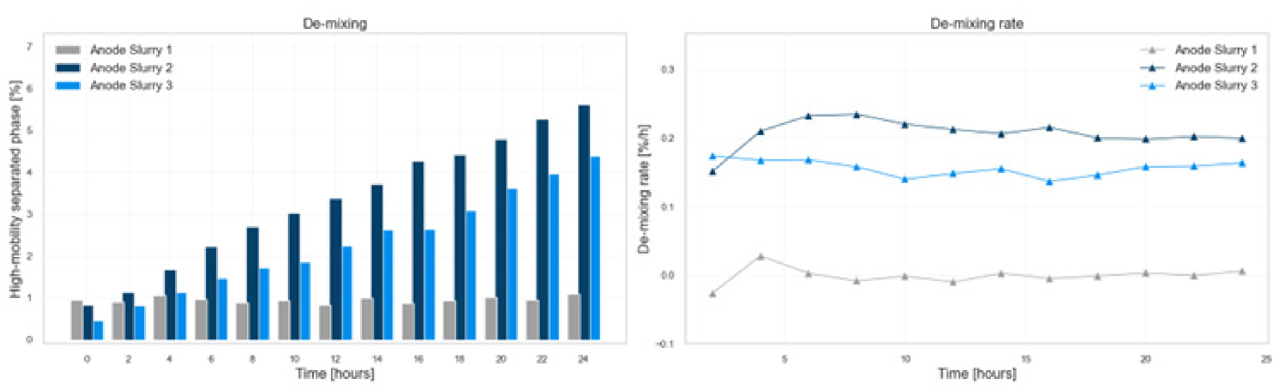


Figure 1 Time stability by TD-NMR in different electrode slurry formulations. De-mixing due to sedimentation [left] and de-mixing rates [right] versus time.

Evaluating physical properties of slurries by TD-NMR

Viscosity and density values for distinct slurry formulations are mainly governed by the physical properties and concentrations of their solid fraction constituents (polymeric binders and carbon-based materials [1,2]) versus solvent content. Temperature-controlled TD-NMR relaxation and diffusion measurements with a Bruker minispec provide a robust set of tools to investigate and characterize different slurry formulations and their impact on rheological properties.
A dilution series of stable Slurry 1 has been prepared by adding different amounts of water to produce a set of slurries with different viscosities. The dilution factor linearly correlates with the averaged NMR Relaxation Rate R_2, which correlates with the concentration of solid particles in the mixture. The confidence interval of this correlation is >99.9% (see Figure 2).

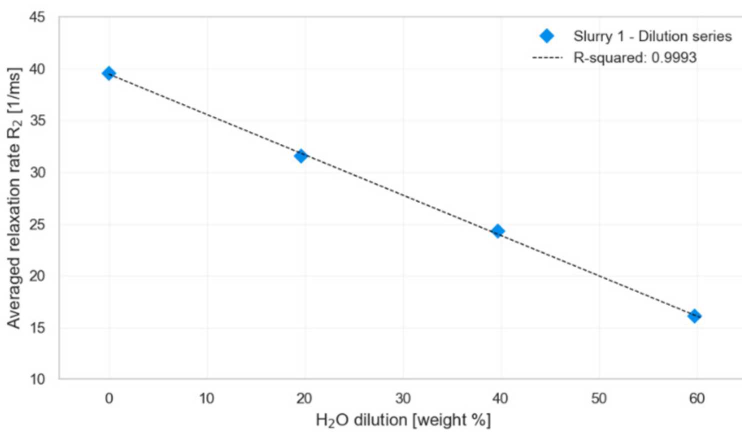


Figure 2 Correlation between the averaged transverse relaxation rate R_2 and the H_2O weight concentration for a dilution series obtained from Slurry 1.

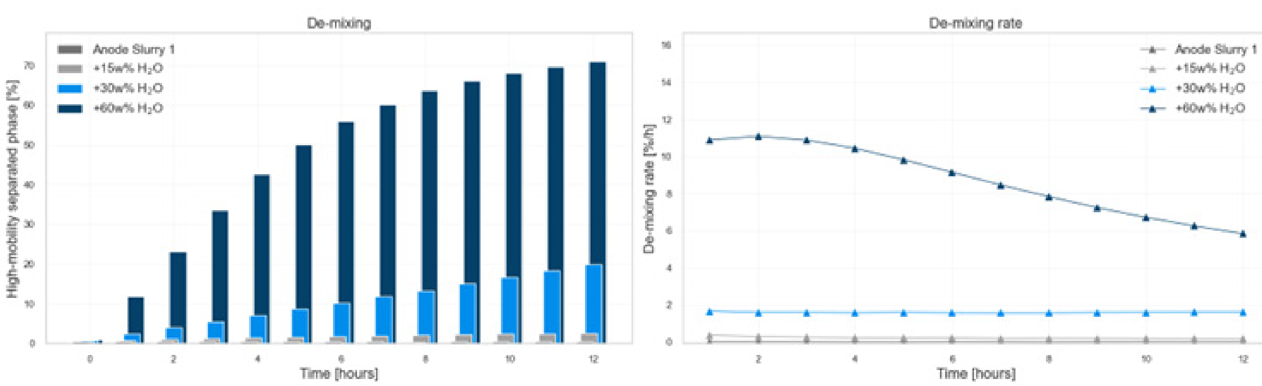


Figure 3 Time stability by TD-NMR in different electrode slurry formulations. De-mixing due to sedimentation [left] and de-mixing rates [right] versus time.

The altered viscosity of Slurry 1 is leading to significantly different stability behavior. Adding 15 w% water to Slurry 1 is not changing the de-mixing behavior significantly whereas the addition of 60%, of course, does. Also, the de-mixing rate for the least viscous sample in this series is decreasing over time showing a plateau-like behavior of the system, as for this sample the sedimentation process evolves faster towards an equilibrium.

Conclusion

The Bruker minispec offers a set of fast and robust TD-NMR methods for determining and monitoring stability and other physical properties of battery electrode slurries. Understanding de-mixing and sedimentation timelines of electrode slurries significantly reduce waste in the battery cell manufacturing process.

The new methods can be used in R&D environments to define the optimal slurry formulation matching all performance and process requirements. The new methods can also be used in Process Control environments to quickly assess the current state of any given electrode slurry prior to the coating process. The rapid and accurate assessment of a current batch of slurry in manufacturing can be done significantly before any visual inspection would be possible.

This new method reduces raw material demand and waste, and decreases the production cost per cell. Therefore, the cell manufacturer gains a competitive advantage by increasing production efficiency.

References:

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