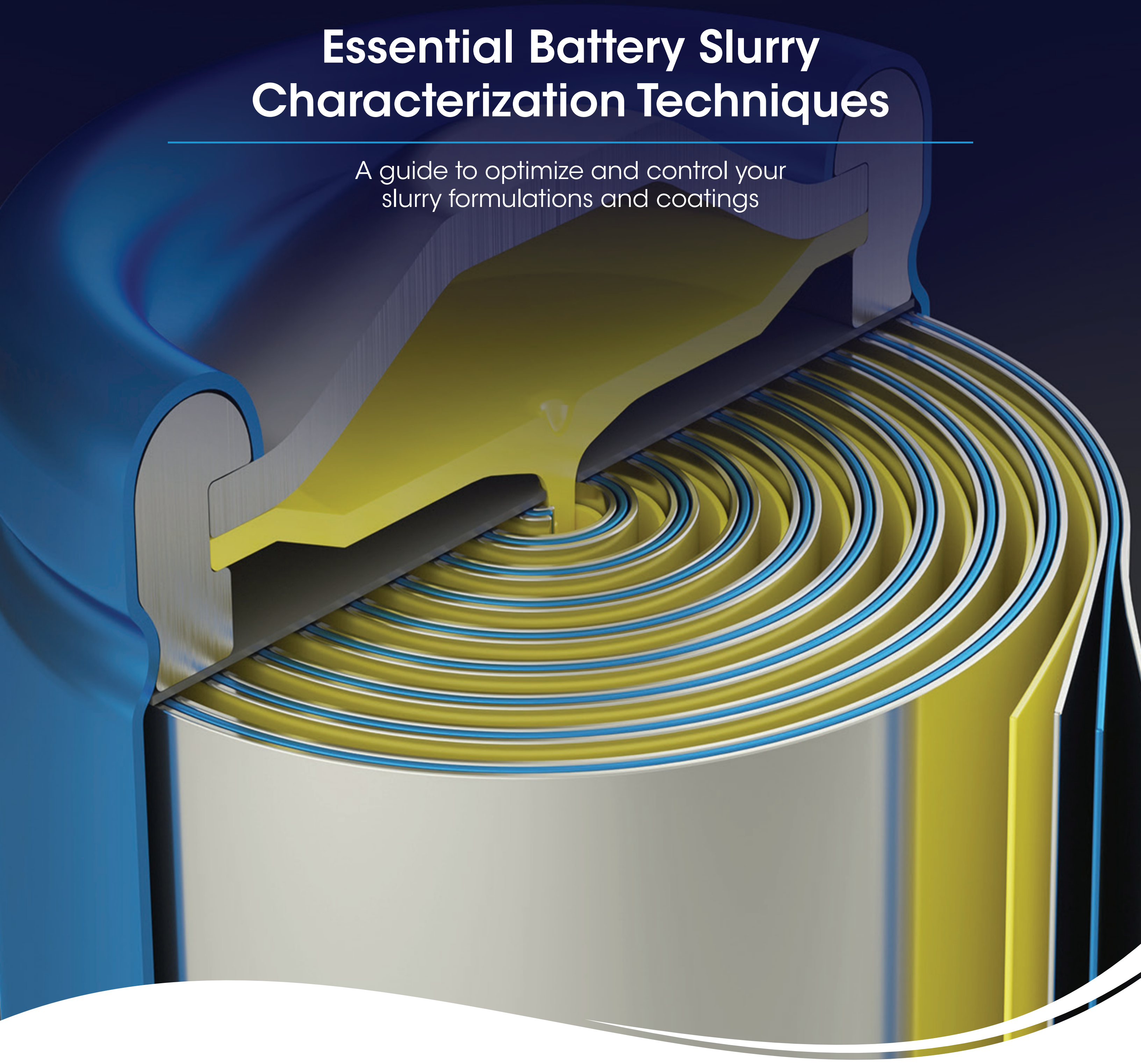
Essential Battery Slurry Characterization Techniques

A guide to optimize and control your slurry formulations and coatings



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INTRODUCTION

Electrode slurries play a critical role in the performance of lithium-ion batteries. These slurries are composed of active materials, binders, conductive additives, and solvents. Their composition and structure significantly influence the performance and durability of the resulting electrodes. Therefore, understanding how to properly mix and coat electrode slurries is essential for optimizing the performance of the battery system.

Analytical techniques such as rheology and thermal analysis are commonly used to characterize the physical properties of electrode slurries. These techniques will help answer:

- How are the slurry properties quantified?
- Will the slurry formulation coat properly?
- How does the slurry structure change during coating?
- Will any changes in the raw materials affect electrode homogeneity?
- What is the shelf life of the slurry?
- How can quality control be assessed?

The studies in this eBook will enable researchers to optimize their formulation and processing conditions for enhanced battery performance.

Rheology is the study of the flow and deformation of materials under stress and plays a crucial role in the development and optimization of electrode slurries. To ensure consistent coating quality it is important to understand rheological measurements, such as viscosity, thixotropic index, and yield stress. Thixotropic behavior, which describes the time-dependent changes in a material's structural deformation, will provide insight into the slurry's structure at rest, how it deforms during coating, and how quickly it will recover after coating.

The electrode slurry matrix will include active powder dispersed within the mix. These powders have a critical role in functionality and battery performance. The shape and size of a powder, however, can alter the way a slurry behaves, from increasing viscosity to ease of dispersing. The study of powder behavior prior to introduction into the slurry can optimize the selection of materials for best compatibility leading to a homogeneous mixture.

Using these techniques to understand slurry behavior and shelf life will help to avoid defects during the drying process. The drying kinetics influence electrode microstructure and should be an important consideration. Understanding the drying temperature, time, and kinetics will help to design the proper drying profile for electrode coatings.

See how today's leading instrumentation helps researchers improve their understanding of electrode slurries and optimizes the manufacturing process to increase speed and reduce scrap.

Our commitment

TA Instruments understands the demands to improve the quality and efficiency of coating materials in the battery industry. We know your research requires accurate, practical techniques to maximize the development period, reduce cost, and expedite time to market.

Access more information about battery specific analysis techniques and solutions HERE.

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Rheological and Thermogravimetric Characterization on Battery Electrode Slurry to Optimize Manufacturing Process

Abstract

Manufacturing electrodes for lithium-ion batteries is a complex, multistep process that can be optimized through the utilization of slurry analysis and characterization. Process optimization requires a thorough understanding of the mixing, coating, and drying conditions of the slurry. In this application note, a **TA Discovery HR rotational rheometer** facilitates coating optimization by measuring slurry viscosity over different shear rates that relate to coating speed. Drying kinetics are investigated with a **Discovery TGA** to yield the most cost-efficient condition. TGA is also employed to determine binder and additive contents for dry electrode quality control.

Introduction

Electrode quality directly contributes to the energy density and electrochemical performance in lithium-ion batteries (LIB). Electrode manufacturing is highly complex, involving mixing the cathode or anode active materials, binder/additive and solvent into a slurry coating on the metal collector, and then drying to remove solvent and calendaring (compacting) the electrode (1). It is essential to optimize electrode processing to obtain high quality electrodes and reduce cost of production (2) (3).

The coating and drying process significantly impacts the quality of the electrode, and thus the performance of the battery. The variable properties of the slurry material, such as aggregate size, shape of the particles, and age dependence, influence the slurry viscosity and coating behavior. If the viscosity of the slurry is too high, it can be difficult to pump and apply homogeneously. Lower viscosity is desirable for increasing coating speed but if viscosity is too low, it may cause dripping issues and result in variation in the coating thickness (2). Analyzing the flow behavior of slurry viscosity under different shear conditions can help optimize the performance of the coating process and is important to study the stability and processability of the electrode slurry.

Once the slurry has been coated on the collector, the solvent must be evaporated from the film. Electrode drying is a complicated process, with three competing physical processes: evaporation of the solvent, diffusion of the binder, and sedimentation of the particles (2). Varing the drying temperature or drying time will result in differences in electrode architecture and electrochemical performance. Drying in different temperatures and measuring the drying kinetics of the slurry material can determine the most efficient drying condition. Once the coating has dried, it is important to check the quality of the product through efficiently evaluating binder and additive contents.

This application note demonstrates a workflow process to optimize electrode coating by determining the ideal viscosity of the slurry coating and the best parameters for drying the electrode. Finally, quality of the resulting dry electrode is assessed through evaluation of the binder and additive contents. The sample used is an anode electrode, with active materials graphite, carbon black, Carboxymethyl Cellulose (CMC) and Styrene-Butadiene Rubber (SBR).

Application Benefits

- Electrode slurry formulation, coating, and drying processes significantly impact quality in electrode manufacturing.
- TA Instruments **Discovery HR-30** rheometer can deliver a sensitive evaluation of slurry viscosity to guide selection of slurry processing conditions during battery electrode manufacturing.
- The HR-30 rheometer measures the shear rate dependent slurry viscosity to optimize the coating process.
- The **Discovery TGA 5500** with sealed pan punch accurately and reliably measures the drying times of the slurry materials at different temperatures to optimize the drying process.
- TGA measures the binder and additive contents to ensure uniform composition and provide quality control of electrode with Pass/Fail feature.

Experimental

The anode slurry and dry electrode were kindly provided by NEI Corporation. The slurry viscosity was measured using a TA Instruments Discovery HR-30 rheometer with the advanced Peltier temperature control system. A 40mm hard anodized aluminum parallel plate geometry was used with a testing gap set at 500 μm. Slurry viscosity was measured from shear rate range of 0.01 1/s to 1000 1/s.

Slurry drying kinetics and quality control of the dry electrode was performed on a TA Instruments Discovery 5500 under inert nitrogen purge gas. Drying is a kinetic process which is directly related to sample thickness and surface area, so it is critical to maintain the same sample volume and size for all the tests. A micropipette was used to enable precise loading of 20 μl of slurry sample loaded on TGA aluminum sealed pan for the drying studies. The sealed pan was used to prevent solvent evaporation. The sealed pan pouched open right before loading for TGA testing. The sample was heated to drying temperature and isothermal for 15 min. To determine the binder and additive content on dry electrode, the electrode sample was ramped 10 °C/min from room temperature to 1000 °C on a platinum pan.

Results and Discussion

Slurry Viscosity

Understanding the formulation stability and flow behavior of the battery slurry is critically important for electrode manufacturing. Some manufacturers choose to use a low-end viscometer with single point analysis, which is not sufficient becasue it cannot fully reflect the flow property of the slurry. Two formulations may have the same viscosity at a single point shear rate, but they can have significant differences in their stability and coating performance. Slurries are shear thinning, its viscosity decreases with increasing shear rates. Figure 1 shows the rheological viscosity testing results of a battery anode slurry over a wide range of shear from 10^{-2} to 10^{3} 1/s, representative of the die slot coating process used in electrode manufacturing. The testing results indicate that this slurry exhibits shear thinning behavior. Table 1 shows the summary slurry viscosity over the shear rates, which provides important guidance to slurry formulation and the coating processing conditions. A good formulation should have a lower high-shear rate viscosity, which ensures an easy and homogeneous coating on the collector; while remaining a higher low-shear rate viscosity to ensure slurry stability (2).

Due to the correlation between shear rate and coating speed (2), these viscosity measurements can be used to guide slurry coating applications. Additionally, viscoelasticity and thixotropy can also measured by HR rheometer (4) to provide useful insights in electrode slurry structure and stability during the coating to further enhance the electrode quality (5). Further details of the viscoelasticity and thixotropy are discussed in the TA Application Note RH119.

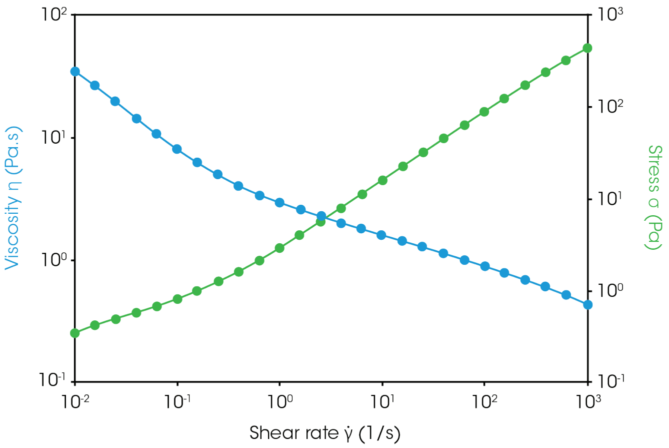


Figure 1. The viscosity of anode slurry over a wide range of shear rate

Table 1. Summary of slurry viscosity at different shear rates

Shear Rate (1/s)	Viscosity (Pa.s)
0.01	34.9
0.1	8.1
1	2.9
10	1.6
100	0.9
1000	0.4

Drying Time

Electrode formulation, coating thickness, drying temperature, and drying rate determine the electrode's drying kinetics. Drying kinetics influence electrode microstructure and should be an important consideration when optimizing the drying process in electrode manufacturing (6). TGA provides a quick test to evaluate the time of the drying process and drying kinetics; the data provide information on drying temperatures and drying times that can guide toward the most cost-efficient drying process.

Figure 2 shows the drying time required for the slurry at different temperatures. Drying kinetics can also be determined from the data (7). Table 1 summarizes the minimum required drying time at different drying temperatures. The results show that the drying time can be reduced from 6.96 min at 90 °C to 3.80 min at a higher temperature of 120 °C.

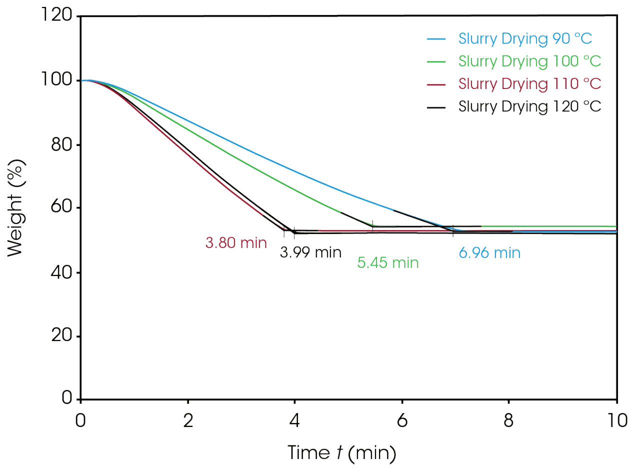


Figure 2. Drying time of the electrode slurry

Table 2. Minimum drying time at different drying temperature

Drying Temperature (°C)	Drying Time (min)
90	6.96
100	5.45
110	3.99
120	3.80

Binder and Additive Contents

After the electrode is dried and calendared, it is important to confirm the electrode is uniform with even distribution of binder and additive to ensure good adhesion, maintain flexibility, and prevent chipping of the electrode. TGA measures CMC and SBR content, with the highly sensitive Discovery TGA 5500 able to measure µg level weight loss from the dry electrode (Figure 3). The first weight loss peak at 285 °C indicated the CMC 0.70% weight content. The second weight loss peak at 404 °C indicated the SBR 1.88% weight content. The residue at 600 °C indicated 97.42% of the inorganic content. These results can be utilized in quality control to determine if the electrode passes or fails quality measures.

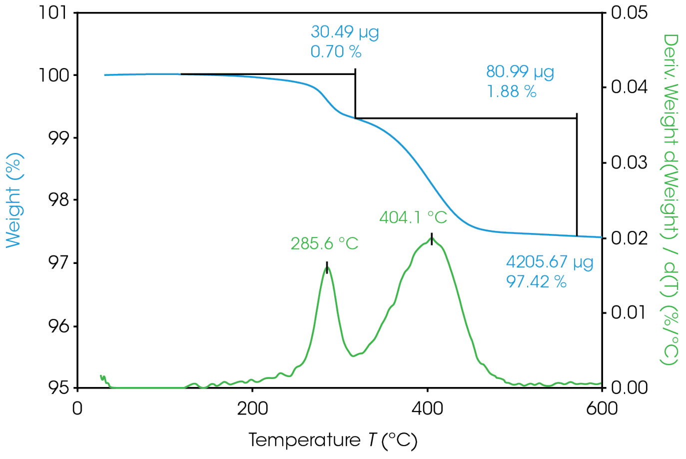
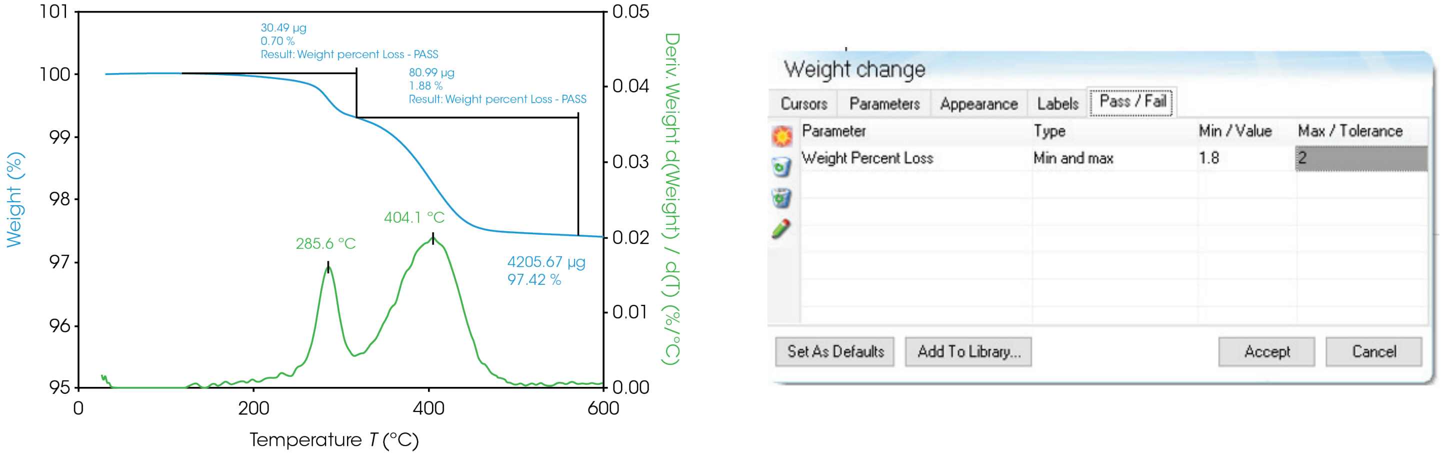


Figure 3. TGA weight loss data of dry electrode

Pass/Fail Feature for Quality Control

In electrode manufacturing quality control, the pass or fail decision must be made immediately to ensure the electrode quality and meet production needs. TRIOS software Pass / Fail feature helps operators to interpret the data and make a faster Pass or Fail decision. The Pass / Fail option determines if the results of the analysis passed or failed the user-defined parameter values. The parameter can be defined as Minimum/Maximum, Value ± % tolerance, or Value ± tolerance. Figure 4 provides an example of the Pass / Fail setting on weight percent loss where the value within Min and Max value of 1.8 and 2.0. When the result is within the min and max value, the analysis will stamp the graph with "PASS" or stamp "FAIL" when the value is outside of the range. The pass/fail feature in TRIOS allows fast Pass/Fail determination for quality control.



Weight change

Parameter	Type	Min / Value	Max / Tolerance
Weight Percent Loss	Min and max	1.8	2

Figure 4. Charted Data and TRIOS Pass/Fail feature for quality control

Conclusion

Electrode manufacturing needs to increase production and reduce cost to meet the high LIB demand. TA Instruments rotational rheometer and TGA provide the essential characterization workflow to optimize cost-efficient electrode manufacturing. The business benefits of the Discovery HR-30 rheometer and the Discovery 5500 TGA include:

- The Discovery RH-30 rheometer measures the flow viscosity of electrode slurry over a wide range of shear rates. This technique is critically important to guide the coating process.
- The Discovery TGA studies the drying kinetics in various drying temperatures that can guide and optimize the most cost-efficient drying condition.
- The sealed pan punch system on TGA prevents solvent evaporation, enabling accurate and reliable measurement of slurry drying.
- The highly sensitive microbalance on the Discovery TGA measures the binder and additive contents on the single layer electrode to ensure uniform composition for quality control.
- The Pass/Fail feature in TRIOS software provides fast pass/fail decision for manufacturing quality control.

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Rheological Evaluation of Battery Slurries with Different Graphite Particle Size and Shape

Abstract

Battery slurry processing is one of the key steps in battery manufacturing that can significantly influence battery performance. The slurry suspension includes multiple components such as active cathode/anode materials, binder and additives etc. mixed in solvent. Differences in slurry formulation can have a big impact on a slurry's stability and flowability. This application note discusses how to use rheology to evaluate the influence of graphite particle size and particle shape on the rheological behavior of a battery slurry. A TA Instruments rotational rheometer was used for the rheological analysis. The measurement results provide quantitative differentiation between two slurry samples with different types of graphite on their viscoelasticity, yield stress, and thixotropic behaviors. The difference in flow viscosities over a wide range of shear rates is also discussed in detail.

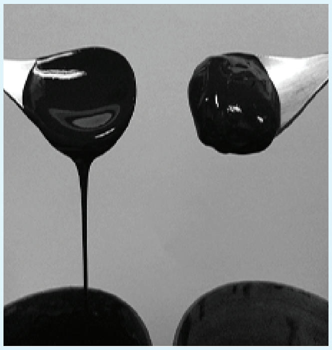
Introduction

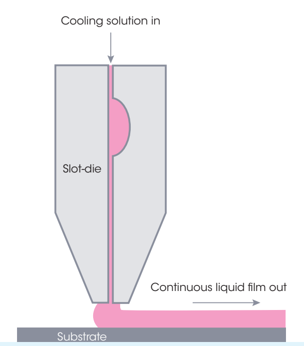
Electrode quality directly contributes to energy density and electrochemical performance in Lithium-ion batteries. Optimizing electrode processing is essential for obtaining high quality electrodes and reducing cost (1), (2). Electrode manufacturing is a highly complex process that involves mixing the cathode or anode active materials, binder/additive and solvent into slurry, followed by coating the slurry on the metal collector, then finally drying to remove solvent and calendaring the electrode (3). Slurry rheology is important for optimizing the coating process and ultimately the quality of the electrode, and thus the performance of the battery.

The formulation and the manufacturing process of slurry suspensions have a substantial influence on their stability and flow behavior. Therefore, slurry production will greatly impact applications such as die slot, doctor blade, comma bar reel to reel coating (3). Rheology provides a powerful technique for analyzing the viscosity and viscoelasticity performance of battery slurries. In this application note, a TA Instruments Discovery HR-30 model rheometer is used for measuring two battery slurries with the same formulation but different types of graphite: natural graphite and synthetic graphite. Natural graphite traditionally has been used to reduce the cost compared to synthetic graphite (4). The measurement results provide helpful guidance for slurry manufacturing and material selection.

Application Benefits

- A slurry's rheological properties are critically important when studying stability and processability for electrode manufacturing.
- A TA Instruments Discovery HR-30 rheometer provides guidance in slurry processing during battery electrode manufacturing by delivering a sensitive evaluation of the viscosity and viscoelasticity of battery electrode slurries
- Rheology can sensitively differentiate the difference between natural and synthetic graphite formulations, which contain different particle sizes and shapes.
- The dynamic frequency sweep test measures sample moduli (G′, G″) and complex viscosity, and helps to compare sample viscoelasticity and network structure.
- Thixotropy analysis measures the shear thinning properties of the slurries and also quantifies the sample structure recovery.
- The flow test can measure samples' yield stress. It also provides the viscosity information of the slurry over a wide range of shear rates.





Experimental Setup

Two battery slurry samples were kindly provided by NEI Corporation. These two samples had the exact same formulation but used different types of graphite: Natural vs. Synthetic. A Scanning Electron Microscopy (SEM) analysis was conducted using a Phenom XL SEM from ThermoFisher Scientific. The SEM images demonstrated the differences in particle size and shape between these two types of graphite. The rheological measurements were performed using a TA Instruments Discovery HR-30 rheometer with the advanced Peltier temperature control system. A 40mm hard anodized aluminum parallel plate geometry was used with a testing gap set at 500 µm. Both slurry samples were sonicated for 15 minutes, and then vortex mixed thoroughly before conducting any rheological measurements. The viscoelastic properties of the slurries were measured using a dynamic frequency sweep procedure. The frequency range was set from 0.1-100 rad/s using a small oscillation amplitude, which is within the linear region of the sample. The yield stress of these two slurries was monitored using a shear rate step down method. The testing shear rate was decreased from 10 1/s to below 0.001 1/s, and the changes of the sample viscosity and shear stress were recorded during the measurements. The thixotropy and thixotropic recovery properties of the slurries were evaluated using a three-step flow procedure, which is demonstrated in figure 1. In the first step, the sample was sheared at a low shear rate of 0.1 1/s. Then the shear rate was increased to 10 1/s in the second step. The changes of the viscosity were recorded. In the third step, the shear rate decreased back to 0.1 1/s. The recovery of sample viscosity was monitored as a function of time.

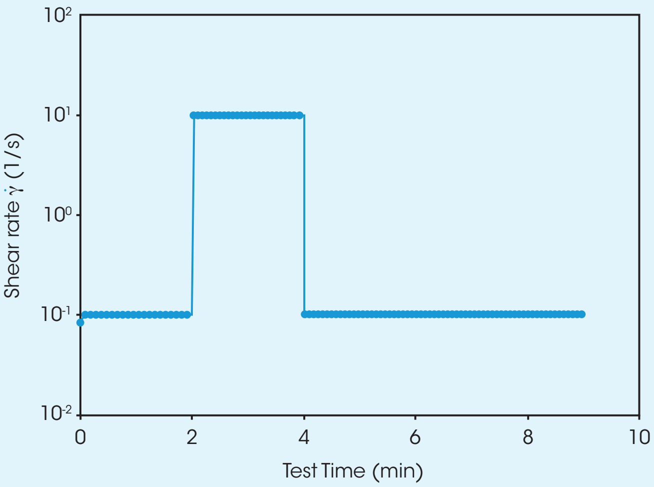
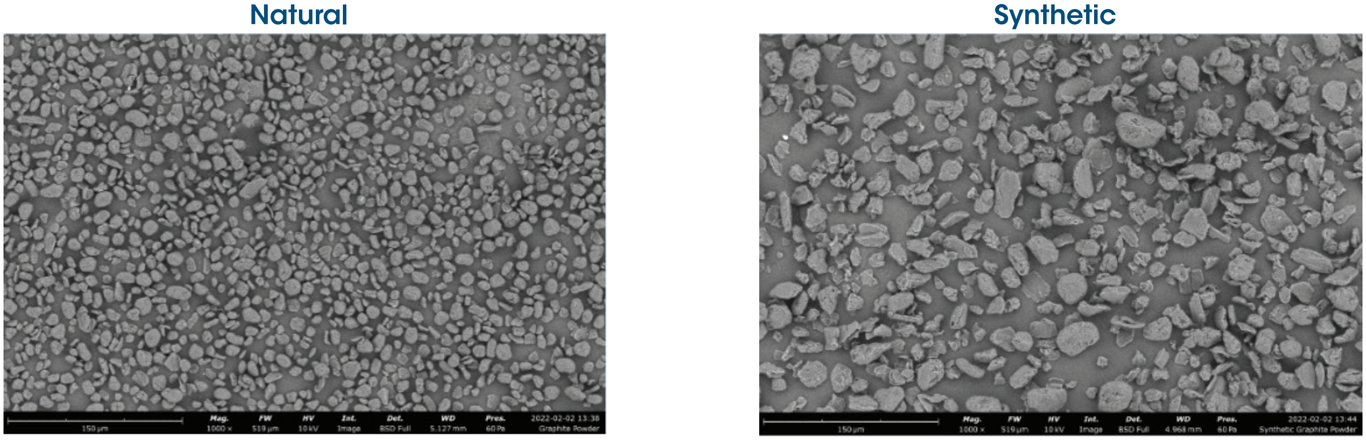


Figure 1. Schematic of a three-step thixotropy measurement program.

Finally, a steady state flow test procedure was used to evaluate and compare the flow behavior of these two slurry samples. The measurement shear rate was programmed from 0.01 to 1000 1/s, which included the shear rate conditions required in slot coating applications.

Results and Discussion

Figure 2 shows the images of natural and synthetic graphite that were used in the slurry formulations. The images clearly illustrate that the average size of natural graphite particle is smaller than the synthetic graphite. Also, the natural graphite particles show more uniform size distribution, and the particle shape seems round and regular. The synthetic graphite particles are larger and also show more irregular shapes with wider size distribution. In slurry formulation, these differences in graphite particles lead to obvious differences in their rheological behavior, which are discussed in the following sections.


Natural

Synthetic

Figure 2. Scanning Electron Microscopy (SEM) images of the natural and synthetic graphite.

Viscoelasticity

The viscoelastic properties of the slurries were measured using a dynamic frequency sweep test. Results are shown in figure 3. In a frequency sweep measurement, when G″ is observed greater than G′, it means that the sample behaves mostly liquid-like with less structure. When G′ is observed greater than G″, it means that the sample is solid gel-like with stronger and more stable structure.

From both frequency sweep test results, one can observe a G′/G″ crossover within the measurement frequency range. At high frequencies, G″ is greater than G′, which means both samples behave more liquid-like. While at low frequencies, both samples behave more gel-like. The G crossover frequency for the synthetic graphite slurry appears at 0.84 rad/s, which is lower compared to the G crossover observed in the natural graphite slurry (i.e. 1.44 rad/s). The G′ curves for both samples turn to reach a plateau at lower frequencies, indicating that the sample started to form a weak structure network. The G′ plateau of the synthetic graphite slurry is lower compared to the natural graphite slurry, which means it exhibits a weaker structure. This is also proved from the yield stress analysis in the following test.

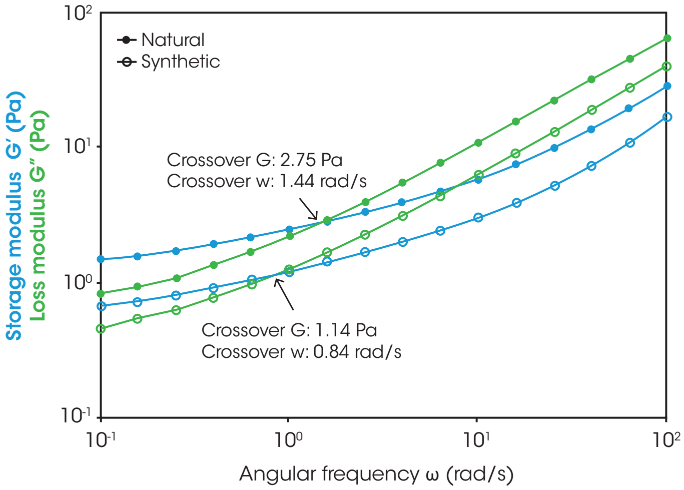


Figure 3. Dynamic frequency sweep tests on Natural and Synthetic graphite slurries at 25°C.

Yield Stress

A yield stress in rheology is defined as the applied stress at which irreversible plastic deformation is first observed across the sample. In theory, yield stress is the minimum stress required to initiate a flow. Yield analysis is important for all complex structured fluids. It helps to better understand product performance such as shelf life and stability against sedimentation or phase separation.

There are multiple rheological methods, which can be used to determine yield stress (5). In this study, the yield stress analysis was conducted using a shear flow ramp down method (results shown in figure 4). From the test results, one can see that under moderate shear rates, the shear stress decreases with decreasing shear rate. But when the shear rate reduces further, the stress curve turns to reach a plateau and becomes independent of rate. This plateau stress value is described as the yield point. Concomitantly, the measured "apparent viscosity" curve goes to infinite with a straight line versus shear rate at slope of -1.

Since the synthetic graphite has a larger particle size and more irregular particle shape in formulation, the slurry exhibits a lower yield and weaker network structure. Hence, this synthetic graphite slurry sample will more easily undergo settling and phase separation. Slurry settling will lead to inhomogeneous distribution of active materials on the electrode and thus reduce battery performance (1).

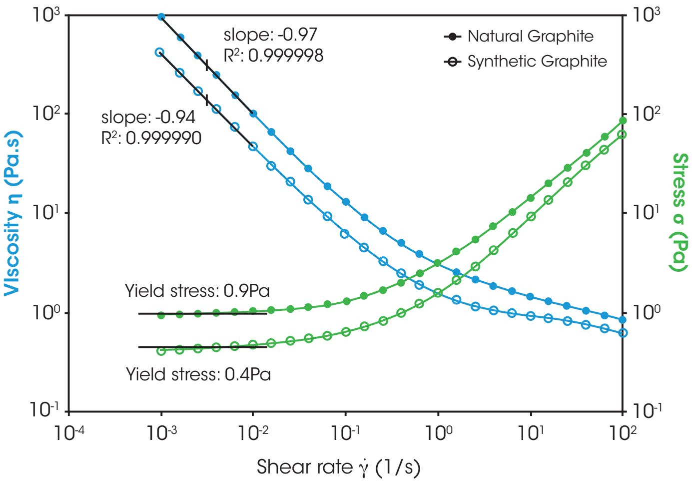


Figure 4. Yield stress measurements on 2 battery slurry samples with different type of graphite. T= 25°C

Thixotropy and Thixotropic Recovery

Thixotropy is a time-dependent shear thinning phenomenon (6). The thixotropic properties of these two slurry samples were analyzed using a three-step flow method (Figure 5). The thixotropic index, which is also called the shear thinning index, is defined as the ratio of the viscosity measured between the low shear (step #1, 0.1 1/s) and high shear (step #2, 10 1/s). The higher the ratio, the more shear thinning this sample is. The third flow step is designed to monitor the sample structure recovery over time. In the third step, the sample was sheared at a low rate (i.e. 0.1 1/s), and the viscosity change is measured as a function of time. In general, the thixotropic recovery is described as the time when sample viscosity recovers back to a certain percentage (e.g. 50% or 80%) of the initial viscosity in the first step.

The thixotropy of the slurry has great impact on the coating and drying of the electrode and thus the electrode quality (7). The comparison of the thixotropic properties between these two battery slurries is summarized in table 1. Within the shear rate range defined in the test, the slurry sample with the natural graphite is more shear thinning compared to the slurry sample containing synthetic graphite. Also, the recovery time for the synthetic graphite slurry is longer than the recovery time for the natural graphite sample. This thixotropic recovery analysis helps to predict sample stability. After shear, if the sample requires longer time to recover its structure/viscosity, then this sample potentially should more easily undergo phase separation, precipitation or settling.

Table 1. Summary of thixotropic index and thixotropic recovery on the 2 battery slurries with different type of graphite

	Natural Graphite	Synthetic Graphite
Thixotropic Index	4.4	3.3
Thixotropic recovery time at 80% (min)	1.2	4.1

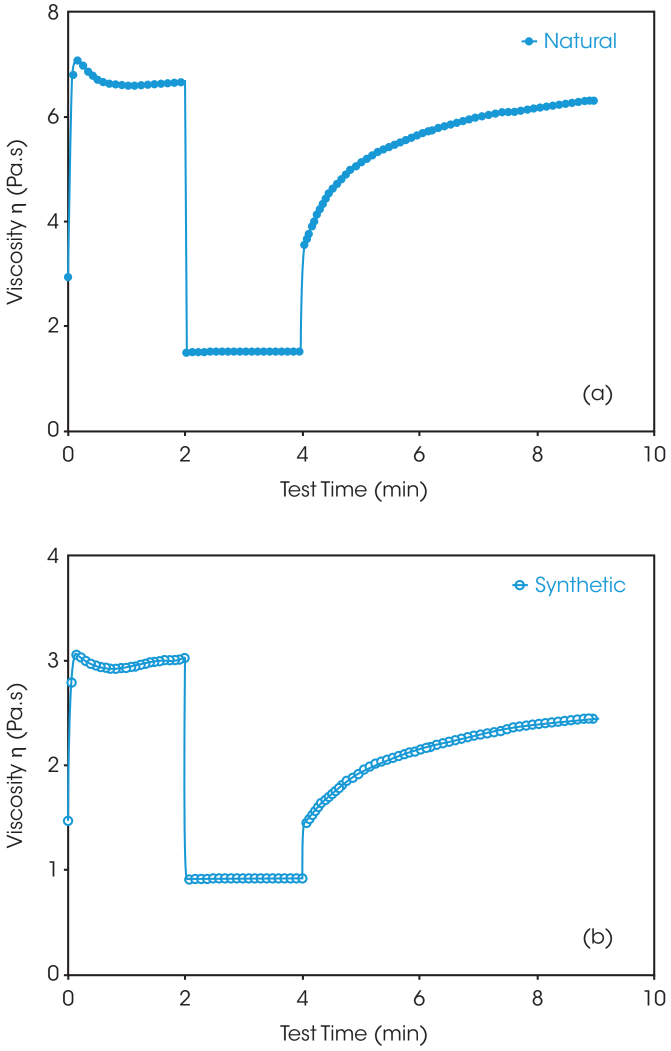


Figure 5. A three-step flow test to evaluate the thixotropic behavior of battery slurries with natural and synthetic graphite. (a) with natural graphite; (b) with synthetic graphite

Flow Behavior

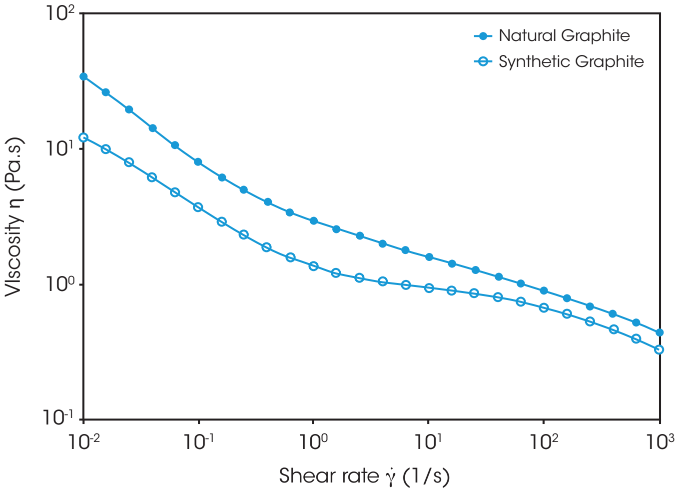


Figure 6. The viscosity comparison of the two battery slurries containing natural and synthetic graphite.

The flow viscosity measurement over a wide range of shear rate is important to study the stability and processability of the electrode slurry. A good formulation should have a lower high-shear rate viscosity, which ensures an easy and homogeneous coating on the collector; while remaining higher low-shear rate viscosity to ensure slurry stability (1). Figure 6 compared the viscosity differences of these two battery slurries over a wide shear rate range (i.e. 0.01 1/s to 1000 1/s). The results show that the slurry containing synthetic graphite, which has slightly larger particle size and irregular shape, has a lower shear viscosity compared to the slurry containing natural graphite, which has smaller particle size and more regular round shape. Under low shear rates (i.e. 0.01 – 1 1/s), both slurries are shear thinning. Within medium shear rate range (i.e. 1-100 1/s), the natural graphite slurry seems to be more shear thinning compared to the synthetic graphite slurry. This is also proved from the thixotropic tests in the previous section. But under high shear rates (100-1000 1/s), both samples are shear thinning again. The die slot coating process is conducted at a shear rate of a few hundreds to a few thousands reciprocal seconds. Therefore, these viscosity measurement results at high shear conditions can be used to guide the slurry coating applications.

Conclusions

Graphite has been widely used in battery manufacturing. The graphite particle size and shape considerably influence the rheological properties of its formulated slurry. TA Instruments rotational rheometer provides the most sensitive evaluation of viscosity and viscoelasticity properties of battery slurries. This application note has compared the rheological properties of two battery slurries, which were manufactured using different types of graphite (natural vs synthetic). The rheological measurement results quantitively compared the differences of their viscoelasticity, yield stress, thixotropic behavior, and the flow viscosities over a wide range of shear rates. The insights of these rheological measurements include:

- Dynamic Oscillatory test: Studies the viscoelastic properties, which help to compare formulation structure and stability.
- Yield stress: Helps to predict storage settling, which could lead to inhomogeneous distribution of active materials on the electrode and thus reduce battery performance.
- Thixotropy and thixotropic recovery: Studies the shear thinning and structure recovery of the formulation after shear. If one formulation requires longer time to recover its structure/viscosity, then it can potentially more easily undergo phase separation, precipitation or settling which may impact the coating and drying of the electrode and thus the electrode quality.
- Flow viscosity: Viscosity studies over a wide range of shear rates are critically important to guide the die slot coating process.

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Powder Rheology of Graphite: Characterization of Natural and Synthetic Graphite for Battery Anode Slurries

Introduction

Lithium-ion battery performance relies heavily on well formulated electrodes consisting of active material, binder, and other additives. Powder properties are an important consideration in traditional slurry or dry processing techniques for electrode manufacturing. For lithium-ion anodes, the most common active material is graphite, due to its high energy density, power density, and long cycle life. Its abundance and low-cost result in it dominating the anode market [1]. Graphite may originate from natural or synthetic sources. Synthetic graphite is typically manufactured by subjecting amorphous carbons to high temperature for extended periods of time. This process provides energy for the slow graphitization phase transition. Synthetic graphite has superior purity, thermal expansion, and thermal stability compared to natural graphite; however, natural graphite is cheaper [2]. Manufacturers may blend or use either source of graphite in their applications and quantifying powder behavior can help with optimizing manufacturing processes or designing hoppers [3].

Powder shear strength and cohesion impact the properties and performance of the final graphite slurry. When a powder has high cohesion, aggregates may form during storage and result in an inhomogeneous slurry. These particle aggregates may cause defects in the anode coating, which can result in battery failure. For powders with high yield strength, more energy will be required to flow the powder into the other slurry components for mixing. It is important for manufacturers to be able to quickly check these properties in order to optimize slurry processing. The **Powder Rheology Accessory** for TA Instruments HR Rheometers can be used to characterize cohesion and flowability of graphite powders and the results can be applied to reduce aggregates and achieve flow prior to slurry production. Manufacturers can use this information, combined with other rheology measurements of the slurry such as viscosity, viscoelasticity, yield stress, and thixotropy [4] to avoid anode defects. Through powder and fluid rheology, the HR rheometer provides a complete solution for battery rheology needs from graphite powder to formulated slurries.

Experimental

Synthetic and natural graphite samples from commercial and industrial sources were tested. Commercial samples were purchased from Sigma Aldrich and industrial samples were kindly provided by NEI Corporation. The TA Instruments Powder Rheology Accessory was used with Discovery HR 30 rheometer to perform shear measurements. Duplicate measurements were performed with fresh samples under ambient conditions.

Application Benefits

- Battery manufacturers can characterize graphite from different sources to optimize processing and material handling to avoid defects in anodes.
- Powder shear testing is sensitive to subtle differences in particle morphology and is indicative of behavior under consolidation.
- The Discovery HR allows manufacturers to easily switch between the rheology of slurries and powders.

Powder Shear

Measurements were performed using the shear cell consisting of serrated upper plate and cup (Figure 1) similar to previous work [5] in accordance with ASTM D7891 [6]. The powder was loaded and consolidated at 9 kPa axial stress before trimming the sample as shown in Figure 2. The measurement consists of preshear and shear steps at specified stresses. The preshear normal stress is equal to the consolidating normal stress. The shear stresses were performed in descending order from 7 to 3 kPa at 1×10^{-3} rad/s until steady state was reached as shown in Figure 3. The TA Instruments Powder Analysis option in TRIOS software was used to determine cohesion, unconfined yield strength, and major principal stress [6].

Figure 1. Shear cell with serrated upper plate and cup to prevent powder slip.

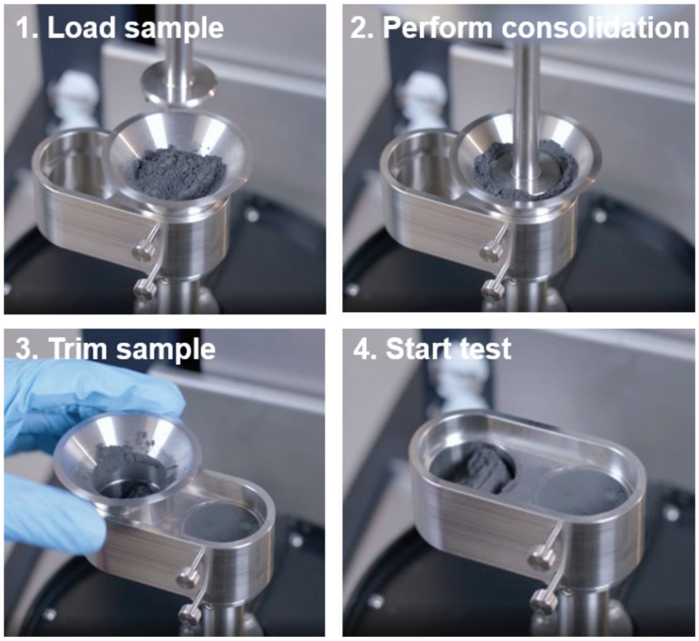
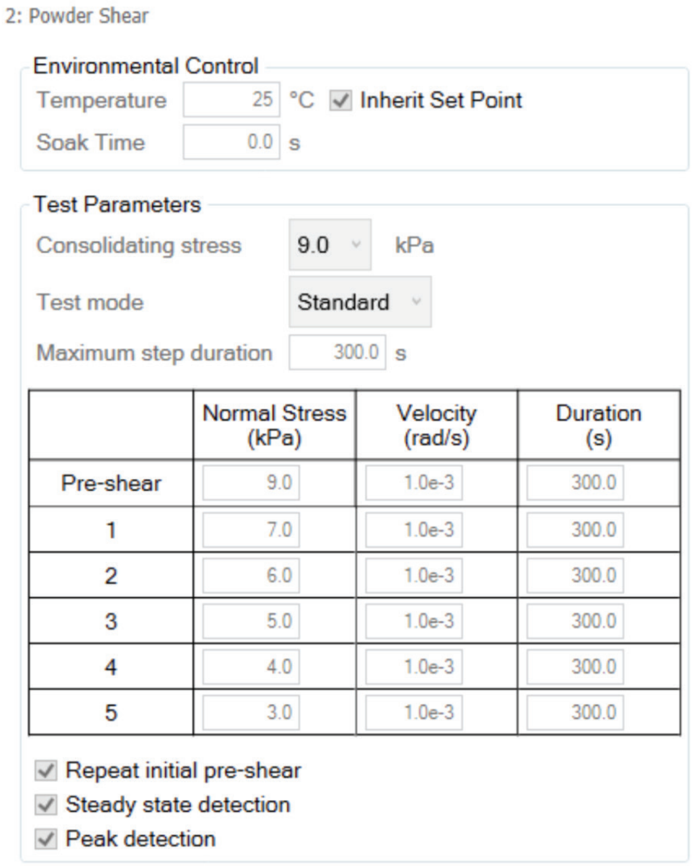


Figure 2. Sample loading and trimming for the Powder Shear Accessory.

Results and Discussion

SEM images of the commercial and industrial graphite samples are shown in Figure 4. The as-received samples vary in terms of particle size distribution, aspect ratio, and morphology. The industrial natural graphite particles are approximately the same size and are rounded with some surface roughness. The commercial natural graphite particles are larger and more angled than the industrial samples. The industrial synthetic graphite has angled and rounded particles with dispersed smaller particles. The commercial synthetic graphite appears to have a large concentration of flake-like particles unlike the industrial sample.

The powder shear results are shown in Figures 5-6. In Figure 5, the results for both types of natural and synthetic graphite are shown. The duplicate measurements show good reproducibility. Figure 6 shows representative data for the yield locus analysis and Mohr's circles, which are used to calculate cohesion, yield strength, and major principal stress. A line of best fit or "yield locus" is drawn through the shear data and extended to the y-intercept. The first Mohr circle is drawn such that it passes through the origin and is tangent to the yield locus line. The second Mohr circle is drawn such that it passes through the preshear average (not shown) and is tangent to the yield locus line. Cohesion is the y-intercept of the yield locus. Unconfined yield strength is the smaller x-intercept and major principal stress is the larger x-intercept.



2: Powder Shear

Environmental Control

Temperature 25 °C ☑ Inherit Set Point

Soak Time 0.0 s

Test Parameters

Consolidating stress 9.0 kPa

Test mode Standard

Maximum step duration 300.0 s

	Normal Stress (kPa)	Velocity (rad/s)	Duration (s)
Pre-shear	9.0	1.0e-3	300.0
1	7.0	1.0e-3	300.0
2	6.0	1.0e-3	300.0
3	5.0	1.0e-3	300.0
4	4.0	1.0e-3	300.0
5	3.0	1.0e-3	300.0

☑ Repeat initial pre-shear
☑ Steady state detection
☑ Peak detection

Figure 3. TRIOS powder shear test parameters.

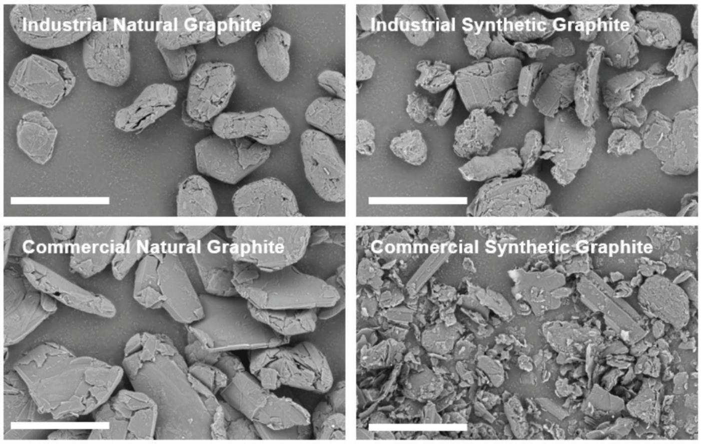


Figure 4. SEM images of commercial and industrial synthetic and natural graphite.

A summary of the powder shear values is shown in Table 1. Higher cohesion indicates that the particles will likely form agglomerates, which will require additional energy to break up. Higher yield strength impacts flowability as the powder will not flow below the yield strength. Higher principal stress corresponds to higher failure force. The commercial natural graphite has the lowest cohesion, unconfined yield strength, and major principal stress of all samples tested. The commercial synthetic graphite has the highest values tested. If a manufacturer relied on both commercial sources of graphite, they would observe significant differences in flow behavior and likely more anode defects for the commercial synthetic powder. The industrial natural graphite has lower values than the industrial synthetic graphite, however the samples are more closely matched as shown by the percent difference. A manufacturer switching between natural and synthetic graphite from the industrial source would be less likely to report issues with mixing, agglomeration, and coating defects.

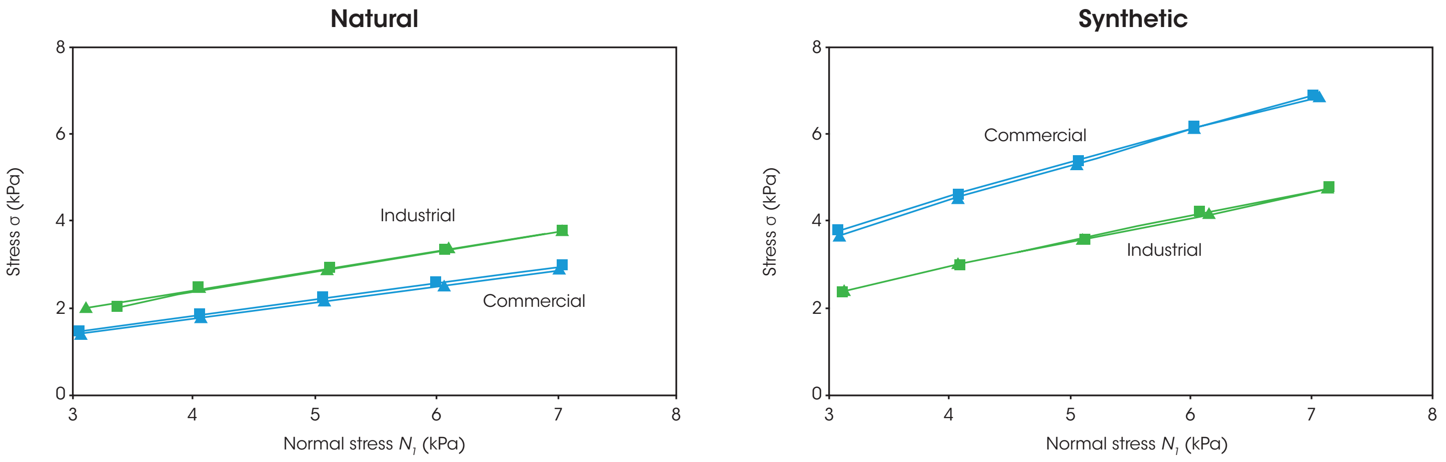


Figure 5. Duplicate powder shear results for industrial and commercial natural and synthetic graphite.

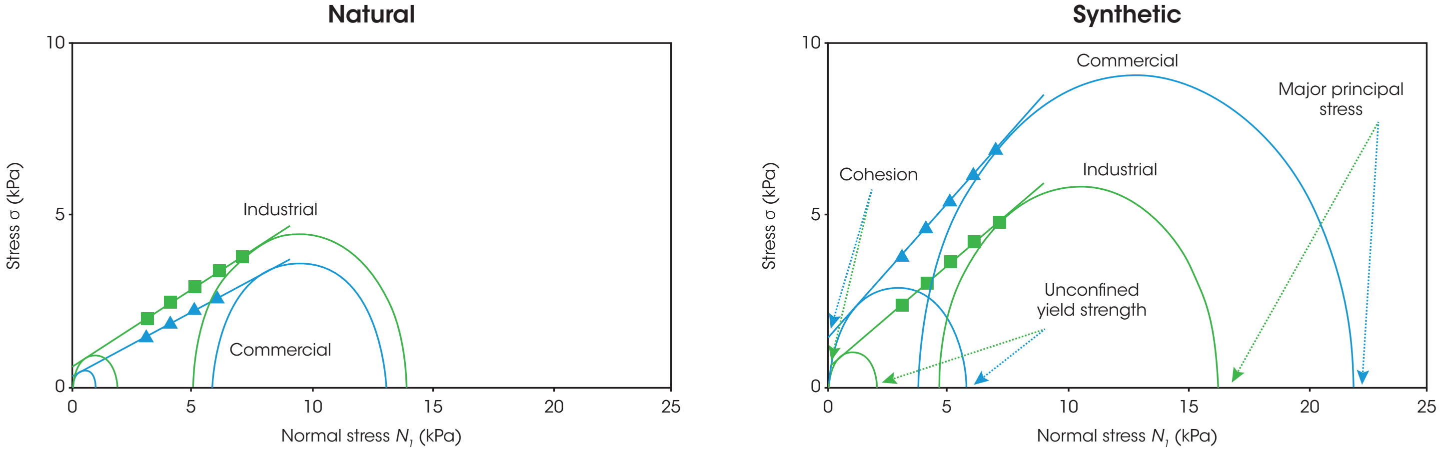


Figure 6. Representative yield locus analyses of commercial and industrial natural and synthetic graphite.

Table 1. Powder shear results for commercial and industrial natural and synthetic graphite with percent difference between natural and synthetic.

	Commercial			**Industrial**		
	Natural	Synthetic	Difference (%)	Natural	Synthetic	Difference (%)
Cohesion (Pa)	310 ± 30	1320 ± 110	326	530 ± 70	610 ± 50	15
Unconfined Yield Strength (Pa)	880 ± 90	5470 ± 400	522	1670 ± 210	2130 ± 150	28
Major Principal Stress (Pa)	12960 ± 100	21980 ± 170	70	13850 ± 60	16250 ± 10	17

Conclusions

Graphite is a key lithium-ion battery anode component. Manufacturers may use natural or synthetic graphite, depending on the application and purity requirements. As demonstrated here, graphite properties can vary significantly between sources and types. Powders with high cohesion and poor flow properties can result in inhomogeneous slurries or dry mixing, resulting in defects in electrodes leading to battery cell failure. The TA Instruments Powder Shear Cell can be used to quantify these differences, to help optimize storage and mixing conditions and screen incoming raw materials.

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Time Dependent Stability of Aqueous Based Anode Slurries with Bio-Derived Binder by Rheological Methods

Abstract

Battery solvents have come under increased pressure and regulation due to their negative environmental impact, forcing manufacturers to identify more sustainable practices. A focus has been on electrode solvents, where much of the battery manufacturing cost is attributed to the resource-intensive solvent drying and recovery process. As companies look toward more environmentally compatible and cost reducing processes, it is critical they understand the impact of new materials to the overall slurry stability and coating process. This application note will investigate the slurry aging and stability through its flow behavior and viscoelastic properties by using **rheological methods**. The slurry studied demonstrates a decrease in stability over time, which can be used to indicate the appropriate batch lifetime in a production environment.

Introduction

Lithium-ion batteries (LIBs) have evolved as the primary energy storage option for a range of applications, from consumer electronics to electric vehicles [1] . While the battery industry is leading the charge in future energy storage solutions, there are still obstacles in the manufacturing processes for batteries. These challenges include reducing manufacturing costs, optimization of components, homogenous and consistent mixing of components, sustainability challenges, and high volumes of intermediate materials such as organic solvent. Government regulations are also increasingly restricting the use of harmful materials. There is currently a significant effort to reduce or replace the common organic solvents used in electrode slurry processing such as N-Methylpyrrolidone (NMP) to achieve manufacturing sustainability and reduce costs [2] . NMP is used for its ability to dissolve polyvinylidene fluoride (PVDF), which is one of the most common binders used in LIBs [3] . The use of the organic solvent and processing of PVDF render this a non-sustainable manufacturing methodology. This limitation has led to the development of aqueous-based slurries that can utilize water-soluble bio-derived polymeric binders while increasing the solids content of the slurry to decrease the amount of solvent needed. A widely used and sustainable choice of binder is carboxymethyl cellulose (CMC) for aqueous based anode slurry formulation. This polymer is derived from cellulose and therefore is environmentally compatible and water soluble at low concentrations.

While the sustainability benefits of CMC aqueous-based slurries are apparent, there are practical concerns that arise with bio-based binder systems. One such consideration is the hydrolyzable nature of bio-based polymers. In CMC, hydrolysis reactions occur as a natural product from the presence of advantageous impurities such as bacteria that can breakdown the polymeric structure. These reactions can result in a structural breakdown of the weak CMC network that stabilizes the dispersion of the active material in the slurry. Rheology is an ideal option to investigate this structure and its subsequent breakdown after processing. The sensitivity of rheological measurements to weak network structures renders it superior to single-point **viscometer testing**, which is usually performed off-line in the battery slurry manufacturing process.

In this note, the stability of a CMC-based aqueous anode slurry is explored as a function of time. The rheological changes over time are critical for the optimal processing of the slurry. For efficient quality analysis and control (QA/QC) testing, determination of viscosity and viscoelastic behavior during the manufacturing process is very important and can be achieved on the **HR series rheometers**.

Experimental

The slurry used in this work is an aqueous-based anode slurry containing graphite, conducting carbon (CC), CMC, and Styrene Butadiene Rubber (SBR). Component concentration was optimized to industrially relevant concentration ratios and prepared with total solids content loading of 59 weight percent (wt.%). High solids content can be utilized to reduce cost and time in the slurry manufacturing process. This reduction in solvent will reduce cost along with drying time and allow higher throughput.

The **anode** slurry used in this work was formulated with raw materials provided by the NEI Corporation. The formulation consisted of 92% natural graphite, 3% CC, 1.5% CMC, and 3.5% SBR as the solids content ratio by weight percent. The SBR was supplied as a 50% dispersion in water. Briefly, the slurry was prepared by adding the CMC powder to a stir-plate and mixing it with the desired water content and the SBR dispersion. This mixture was stirred for eight hours with no added heat to avoid thermal degradation influences. The graphite and CC were then added, and the slurry was vortexed and stirred for another four hours. The slurry used was 59 wt.% solids as determined by **thermogravimetric analysis** using the TA Instruments™ **Discovery™ TGA 5500**.

The **rheological measurements** were conducted using a TA struments **Discovery™ HR30 rheometer.** Frequency sweeps were performed at a low strain (0.1%) that was within the linear viscoelastic region (LVR) from 100-0.1 rad/s [4] . Flow sweeps were performed from 0.01-1000 s-1 with steady state sensing selected in the TRIOS software on the sample after it was aged one, three, four, and seven days. The sample was continuously stirred using a magnetic stirrer for the time point experiments. In addition, the sample was vortexed before each test to ensure a homogenous dispersion and remove any sedimentation effects. All experiments were done with a 40 mm aluminum parallel plate and a lower Advanced Peltier Plate to hold the temperature constant at 25 °C. A test gap of 0.5 mm was used for all experiments.

Results and Discussion

Flow Behavior

To determine slurry viscosity, flow sweep tests were performed. Figure 1 shows the flow sweep data of the slurry that was aged for one, three, four, and seven days. The flow curve of the one-day slurry shows a low-shear viscosity of 132 Pa.s which is followed by subsequent shear thinning behavior. The aged slurries show a drop in the low-shear viscosity to 83.1 Pa.s, 35.7 Pa.s, and 21.4 Pa.s for the samples aged at three, four, and seven days, respectively. These results show that the slurry structures weakened over time. The same shear-thinning behavior is observed and expected as this is the same sample, but with a reduced weak network stability.

Along with shear thinning, the presence of a shear plateau feature in the mid-shear region for all the samples is observed. This indicates, in this specific formulation, that some structural formation or re-arrangement is present when sufficient shear is achieved. This structural rearrangement decreases the degree of shear thinning in the plateau region. Following the plateau, at high shear rates, there is a significant drop off for all four sample viscosities.

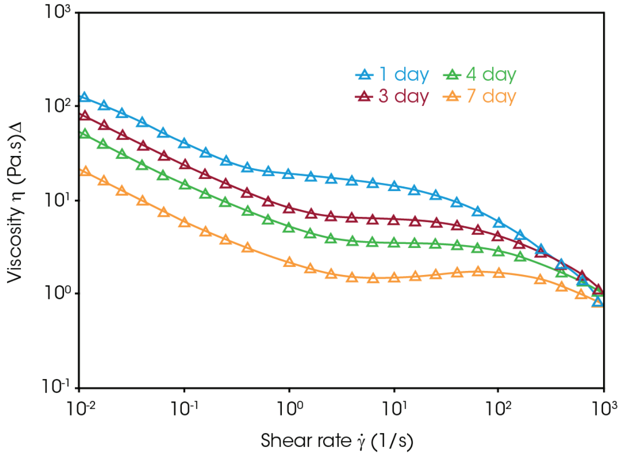

Figure 1. Flow curves of the CMC, SBR, CC, and graphite aqueous anode slurries. The days of aging are shown in the legend.

Due to the high solids content nature of the slurry, the possibility of shear induced structural formation is evident. The polymeric part of this dispersion constitutes 5% of the total slurry. The CMC and SBR act in concert to bind the active materials to produce a concentrated dispersion with an extremely high graphite + conducting carbon amount of 54 wt.%. Prior studies have shown that high solid content aqueous anode slurries demonstrate this mid-shear plateau [5] . This plateau can arise from shear- induced ordering within the slurry where the graphite and conducting carbon have a shear rate dependent ordering within the polymeric network. Another interesting feature is the plateau region appears to shift slightly to higher shear rates as the sample ages. Using the statistical analysis in the TRIOS software, the shift in the mid-point of the plateau regions could be quantified. The shift to higher shear was observed from 2.5, 10.0, 15.8, and 25.1 s-1 for the one-, three-, four-, and seven-day samples, respectively. The observed viscosity decrease can be attributed to an integrity loss of the polymeric structure stabilizing the dispersion. This can lead to the agglomeration of the active component. Changes in the CMC network structure have been shown to play a key role on the microstructure and flow behavior of these aqueous-based slurries previously [6] . This micro-scale structural change will manifest as a shear-dependent phenomenon as observed. From a single point viscometer, this structure change will not be observed.

Viscoelasticity

Viscoelasticity refers to the nature of a material that has properties of a liquid and a solid. For slurries used in battery manufacturing, viscoelasticity is desirable because, at times, it is beneficial for the material to flow and possess liquid-like qualities. At other times, such as after coating, possessing a more solid-like material is desired for the coating to not flow away. The dominating viscoelastic behavior is sensitive to the timescale of the process occurring to the material. Therefore, oscillation frequency sweep tests were used to examine the viscoelastic properties of the slurries.

Figure 2 shows the frequency sweep data for the four samples. Beginning with the high frequency region, the loss modulus (G″) is above the storage modulus (G′) for all the samples. This indicates a more liquid-like behavior. For time points of one, three, and four days, a modulus crossover occurs where G′ becomes greater at lower frequency, indicating a transition to a gel-like structure. This crossover point is related to the change of network structure of the materials, and it is a materials property. As seen in Figure 3, the G′ value at which this crossover occurred decreases to a lower modulus as the samples were aged. At the lowest frequency region, a plateau starts to develop in G′, which is indicative of a weak structure. The G′ of the weak network formed as a function of aging is shown in Figure 3. The sample that was aged for seven days was distinct in that no G crossover was observed, and more liquid-like behavior was present throughout the entire frequency range. This increased flowability can be problematic in the coating process where some structural recovery is desired for proper setting of the coating during drying.

The drop in the low frequency region plateau G′ also shows that while a weak network is forming, the network is losing its structural integrity as the sample ages. This network breakdown translates to a loss in slurry stability. From a QA/QC perspective, this viscoelastic information provides insight into how the slurry will behave while processing. For example, from the data above, a thicker slurry with decreased flowability will be expected for a newly prepared slurry. However, if mixing a more flowable liquid with active material, agglomerations may need to be accounted for in the manufacturing process.

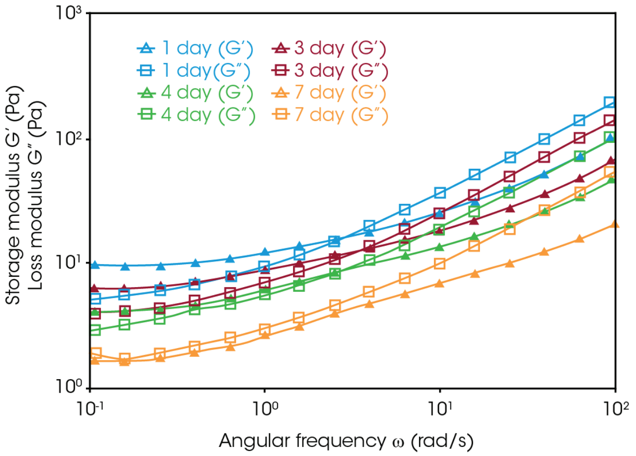

Figure 2. Frequency sweep data of the aged CMC, SBR, CC and graphite aqueous anode slurries. The days of aging can be found in the legend along with (G′) and (G″) modulus identity.

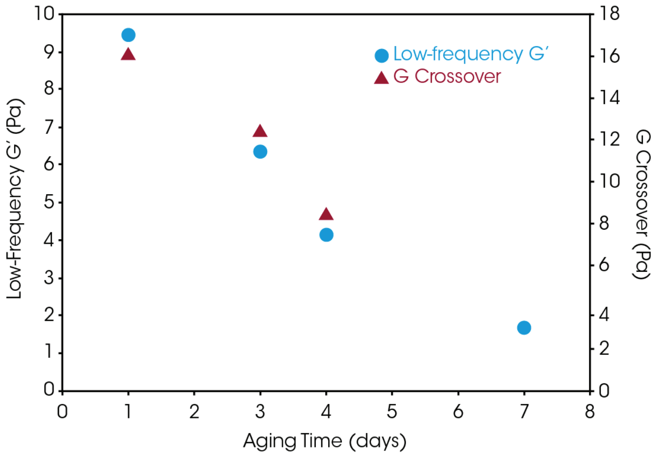

Figure 3. Low-frequency plateau G′ and G crossover trend as a function of slurry aging time.

Conclusions

As governments and regulations push battery manufacturers towards sustainable manufacturing, the use of aqueous-based slurries with environmentally friendly components is desirable. It is necessary to understand the impacts of formulation and processing changes on the slurries to optimize manufacturing. Rheological measurements of a high-solids content battery anode slurry containing a bio-derived binder investigated the impacts of aging on the structure and properties of the slurry. Using a Discovery HR rheometer, it was found that as the slurry aged for up to one week, the viscosity decreased, and the polymeric network integrity weakened. This network stability loss subsequently led to a change in shear-induced agglomeration between the inorganics in the slurry. The sensitivity of the instrument at low shear rates and low frequencies enabled detection of these subtle and distinct rheological property differences, making this a useful tool in QA/QC testing and slurry optimization measurements.

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