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THE BLACK POWDER BEHIND BATTERY POWER

Jeffrey J. Richards and Julie B. Hipp

Carbon black, a key ingredient in ancient inks, is used today to make the porous electrodes found in many rechargeable batteries. Understanding how to control its microstructure can pave the way to better-performing batteries.

The widespread use of rechargeable electronics and the proliferation of electric vehicles are driving an increased demand for high-performance batteries. Both the public and private sectors in the US are investing billions to meet that demand by expanding production of next-generation battery chemistries and technologies. It's projected that by 2028, 1000 GWh/yr of battery-production capacity, enough to power 10 million electric vehicles, will be available.¹ Lithium-ion battery technology leads the way in that endeavor. The batteries contain porous electrodes separated by an ion-permeable membrane. The electrodes are manufactured by coating metal foils with battery slurry, a complex fluid that contains the raw materials that make the batteries function. To reach that 1000 GWh/yr milestone on time, kilometers of electrode material must be coated with defect-free battery slurry every day.

The coating process needs to be carefully controlled to deliver the large volume of electrode slurry material and to keep performance high and costs low. But maintaining that control is a challenge. The battery's performance is affected by both the slurry's formulation, which combines many components—including graphite, metal oxide particles, polymers, and carbon blacks—suspended in liquid, and its processing into the dried porous cathodes and anodes, illustrated in figure 1. Any misstep can lead to defects forming in electrodes during the coating process. The profit margins for battery manufacturing are narrow, so the defective coatings must be quickly identified and removed from the production line. Visible defects are easy to spot. When they are found, the process conditions can be

changed to minimize their effect on production. Invisible defects, however, are the greatest concern, and their elimination is critical to the realization of high-performance batteries.

Invisible defects arise from incorrectly structured porous electrodes with poor electrical connectivity and dead ends that do not allow for easy ion and electron transport. A polymer binder and conductive carbon nanoparticles, including carbon black and also carbon nanotubes and nanofibers in some batteries, form the walls of the pores, and they “wire up” the electrochemically active materials—compounds such as graphite and nickel manganese cobalt oxides that store lithium ions—that are in the electrode. While the polymer binder acts like a glue holding the walls together, the carbon nanoparticles provide the structure of the pores and make them electrically conductive.

Carbon black, the conductive nanomaterial most used in batteries today, is a soot-like nanoparticle. The highly engineered type found in batteries is produced at scale by the incomplete combustion of hydrocarbons. In battery slurries, carbon black forms micron-scale clusters, known as agglomerates, whose size and distribution change based on the slurry formulation and the details of the coating process.

In turn, the electrical connections between the carbon black and the active material depend on the size and connectivity of agglomerates. Those two characteristics are defined during the deposition of the liquid slurry because its flow onto the metal-foil sub-

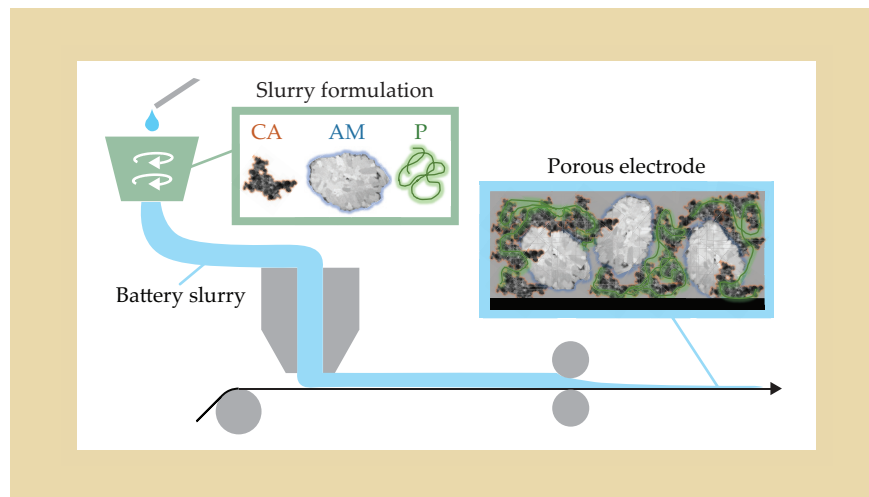


FIGURE 1. POROUS ELECTRODES FOR RECHARGEABLE BATTERIES are built by coating metal foils with a slurry containing conductive additives (CA), such as carbon black; active materials (AM), such as cobalt oxides or iron phosphate, that store lithium ions; and polymers (P) that hold the mix together. The shear applied to the slurry during the coating process alters carbon black's microstructure, which affects the performance of the electrodes.

strate changes the liquid structure. In a future world, quantitative predictions based on the slurry composition and the details of the coating process could lead to the manufacturing of higher-performance battery systems with fewer defects. To realize that vision for efficient mass production, significant advances in scientific understanding of the flow-induced changes of carbon-black suspensions are needed.

Go with the flow

When facing the challenges of controlling carbon-black suspensions, scientists are not without guidance from the past. The flow behavior of those liquid suspensions has been studied for decades, but the control of carbon-black agglomerate size through processing can be traced back millennia. The first example is the use in Asia of soot-based inks, widely known today as India ink. Their earliest development dates back several millennia in China. Those inks, derived from solid bricks composed of carbon black and animal glue, were rehydrated before being used for writing.

A contemporary example is sumi ink, which is made black by incorporating high-quality soot produced from the burning of vegetable oil.² To create it, a dough of soot powder and animal glue is continuously kneaded and folded, sometimes for hours. Kneading is critical to the quality of the ink because the mechanical force it exerts reduces the size of the carbon-black agglomerates and enhances their dispersion, resulting in an even distribution of carbon throughout the dough. The composite is then pressed and dried so that it can be reconstituted with water and used for traditional Japanese calligraphy. Skilled craftspeople are needed to make sumi ink because improper kneading results in poor dispersion of carbon black.

The observation that mechanical force is required to achieve fine dispersion of carbon-black agglomerates is well known in contemporary manufacturing as well. For example, in the production of rubber tires, carbon black is added to improve strength, durability, and longevity.³ Before vulcanization, the molten rubber must be mixed with carbon black and silica nanoparticles by a special machine called a Banbury. It applies tremendous forces to the rubber during the compounding process, during which it breaks up the carbon-black agglomerates and finely disperses them throughout the rubber matrix. The quality of the powder's dispersion is critical because more intense mixing and finer dispersion corresponds to higher performance and longer-lasting tires.

One might intuitively expect that a higher shear force or flow rate in the electrode-coating process will lead to increased dispersion of carbon-black agglomerates in the bat-

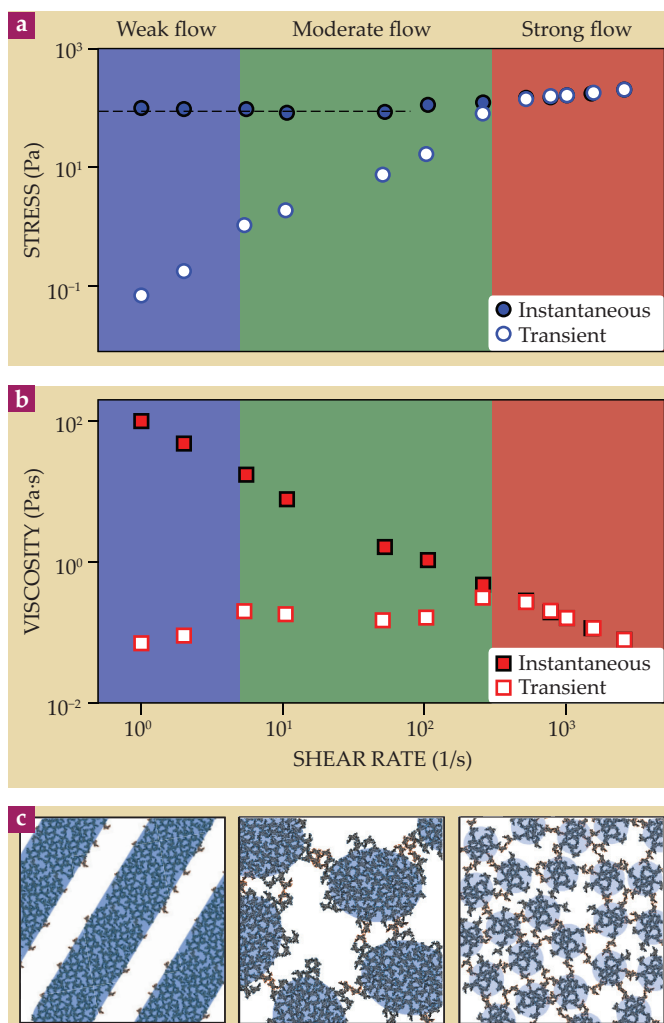


FIGURE 2. FLOW CURVES highlight the three flow regions—weak (blue), moderate (green), and strong (red)—that are commonly observed for carbon-black suspensions and correspond to changes in the material's microstructure. Typical data are shown for the same suspension measured instantaneously (filled symbols) and transiently, after about 1000 s under shear (open symbols), plotted as (a) stress response and (b) viscosity response. A near constant stress response for instantaneous experiments shows that the suspension is solid-like at rest. Decreased viscosity with increased shear rate indicates a shear-thinning property, like that of ketchup. (c) Shear rate-dependent microstructures. In weak-flow conditions, large, anisotropic structures form. Large and small agglomerates develop in the moderate- and strong-flow regions, respectively. (Microstructures are digitally adapted from refs. 4 and 6.)

tery slurry and improved electrode performance. But decades of research have shown a more complicated reality. For that reason, researchers have turned to rheology: the study of the flow-dependent behavior of materials such as paints, cements, and biological fluids.

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With a rheometer, one can measure the force needed to deform a sample at incrementally increasing rates, known as shear rates. From that data, researchers can construct flow curves that summarize the effect of processing intensity on flow behavior for a given material. And they can identify a flow curve's many meaningful features, such as key changes in a sample's viscosity that are linked to changes in its microstructure. Because most viscosity changes occur over finite periods of time, the stress and viscosity of a sample often depend on the length of time spent at each deformation rate. For that reason, experiments are performed that record the response both instantaneously and after longer durations of shear.

Figure 2 illustrates the complex flow behavior of a carbon-black suspension; it shows typical flow curves for the suspension after shorter (instantaneous) and longer (transient, about 1000 s) periods of time at each shear rate. Carbon-black suspensions exhibit a property known as shear thinning, a decreased viscosity at increased shear rates. In coating applications, strong shear thinning can help the liquid flow easily when deformed and stop when the deformation ceases. (Incidentally, ketchup is engineered the same way so that it squirts out of the bottle and slows down when it lands on your food). In suspensions containing carbon-black particles, the shear-thinning behavior observed at high shear rates is often attributed to a breakup of agglomerates.

The instantaneous flow curve in figure 2a shows that a carbon-black suspension exhibits a constant stress at low shear rates. Called a yield stress, it indicates that the material is solid-like at rest. Its magnitude can be used to understand the degree of agglomerate dispersion and the interconnectivity of agglomerates after the flow stops.

Carbon-black suspensions exhibit both shear thinning and yield-stress behaviors, but only in a narrow range of shear rates and often only for particular durations at a given shear rate. Their flow properties can be separated into three regions with distinct microstructural and rheological behavior,⁴ as depicted in figure 2.

In the first region, at low shear rates, the transient viscosity exhibits a nonmonotonic, unpredictable relationship with shear rate. The behavior in that region is difficult to predict because of large-scale anisotropic structures called log-rolling flocs that form because of combined effects from fluid flow and structural confinement.^{4,5}

As the shear rate increases, the log-rolling flocs break up into large, dense agglomerates. In the second, moderate shear-rate flow region, the transient viscosity exhibits a unique rheological phenomenon called rheopexy. The compaction of agglomerates leads to a time-dependent reduction in viscosity with a decrease in shear intensity.

Like wringing out a wet sponge, the densification of agglomerates at those moderate shear rates squeezes out solvent from their internal structure and makes the suspension more fluidlike, with a lower viscosity. Although those large and dense agglomerates do not organize themselves into the log-rolling structures of the weak flow region, it remains unclear if those denser agglomerates are desirable in the slurry and are beneficial to manufacturing. Denser agglomerates, however, settle to the bottom of their container faster than their less dense counterparts, so they may contribute to inconsistencies in the quality of the finished porous electrode.

At high shear rates, in the strong flow region, the flow becomes stable as smaller, more porous agglomerates form.

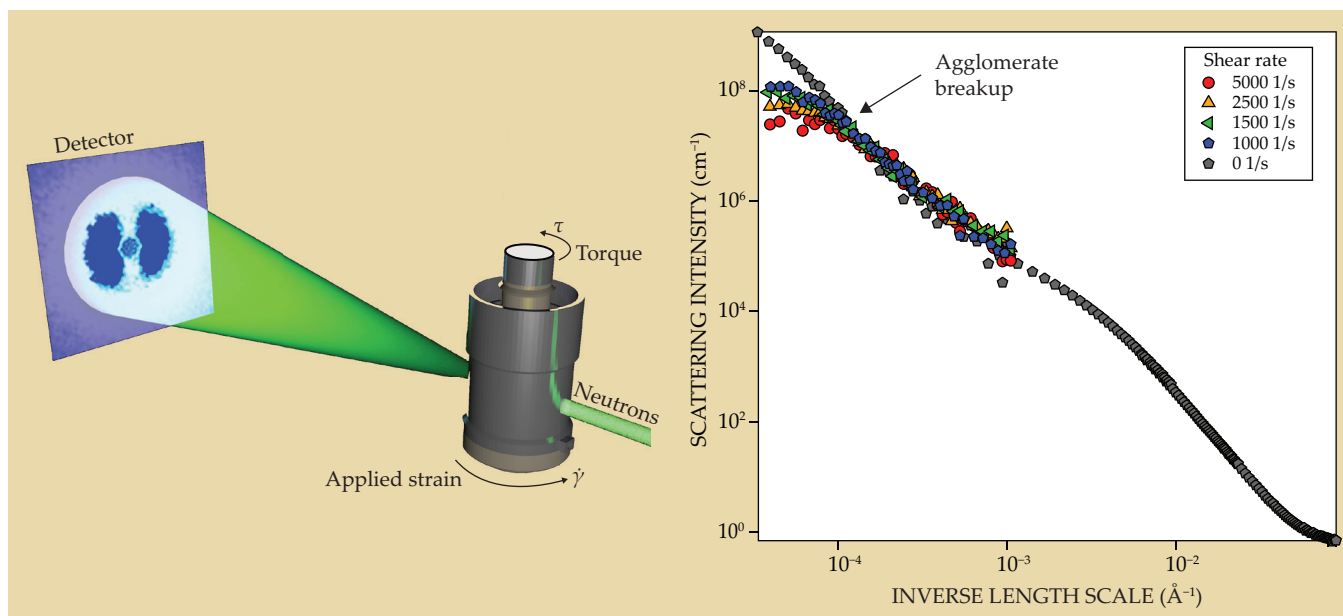


FIGURE 3. SHEAR-DEPENDENT MICROSTRUCTURES are probed by applying shear force to samples in a cylindrical cell that is positioned in the path of the neutron beam from NIST's BT-5 instrument. The drop in scattering intensity at higher shear rates reflects the breakup of carbon black into smaller clusters in the suspension. (Adapted from ref. 8.)

In those conditions, agglomerates break up with increasing shear rate, resulting in a shear-thinning viscosity that does not strongly depend on the duration of the experiment. The extent of agglomerate breakup and the resulting degree of shear thinning are important in the design of electrode-coating processes because of the direct relationship between the speed at which electrode material is coated (shear rate) and properties related to coating quality (slurry viscosity and structure).

But because of the unstable flow and unpredictable nature of the first two flow regions, the region with high shear rate and strong flow is preferred for consistency. While carbon-black suspensions typically exhibit the same three flow regions, the transition between them depends on the formulation details. Recent research has identified the conditions in which the strong-flow region occurs in all carbon-black suspensions: a common transition point at stress responses equal to the yield stress.⁶

Agglomerate breakdown

Although a qualitative understanding of the microstructural evolution in the strong-flow region is currently possible by looking at the flow curve, most quantitative predictions of the agglomerate breakdown remain elusive. Questions about the extent of breakdown and buildup at a given shear rate and whether those processes are reversible have largely remained unanswered because few experimental techniques can look inside those flowing suspensions to examine the evolution of the carbon-black agglomerate structure. For example, adding a microscope to the rheometer can provide access to the macroscale structure, which is tens of microns in size, but it cannot image the micro- to nanometer length scales of the smaller agglomerates because of such limitations as the optically opaque nature of the suspensions and because the length scales are smaller than light can resolve.

In the past 15 years, researchers have used neutron scattering to answer important questions about the flow of soft materials. To gather that data, they placed a rheometer in the path of a neutron beam,⁷ as shown in figure 3. Like an x ray of a hand that shows the bones, neutrons provide a way to examine optically opaque samples over a wide range of length scales that span nanometers to several microns. Those length scales correspond to the changes in the size of carbon-black agglomerates in the rheometer under different shear conditions. That is possible because neutrons move at high speeds and behave like waves. And like x-ray wavelengths, neutron wavelengths are vanishingly small. But unlike x rays, which interact with the electrons in a material, neutrons interact with the atomic nucleus, which makes them uniquely sensitive to hydrogen and carbon atoms, the principal elements that make up carbon black.

That unique property allows for neutrons to easily pass through the metal walls of a rheometer while still interacting strongly enough with carbon-black agglomerate structures to produce a measurable signal. What emerges from neutron-

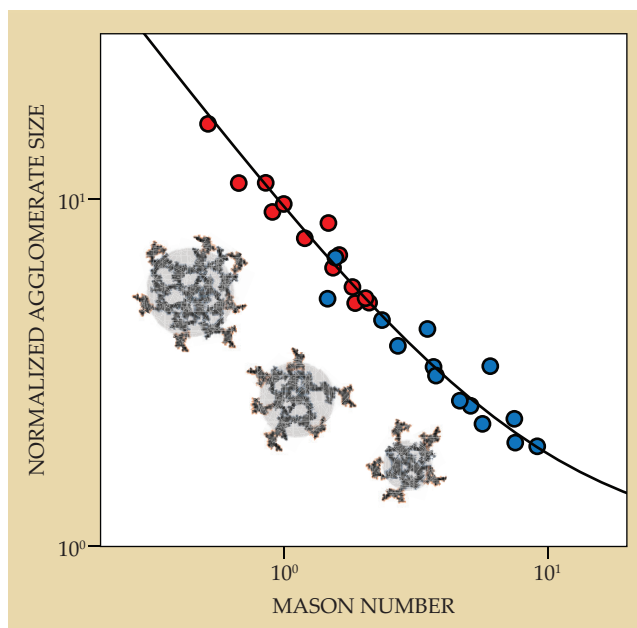


FIGURE 4. THE DIMENSIONLESS MASON NUMBER describes the physics governing the breakup of carbon-black clusters known as agglomerates. The number is a comparison of the shear force that breaks particle bonds with the cohesive force of the bonds. Regardless of the many differences between suspensions, the agglomerate sizes of carbon black in nonpolar (blue) and polar (red) fluids at a range of volume fractions can be predicted just by calculating the Mason number. (Adapted from ref. 9.)

scattering measurements is a pattern that reflects the probability that a neutron scatters at a given angle relative to the incident neutron beam. The scattering angle behaves like a ruler in neutron-scattering measurements, and it is varied to probe a wide range of structural length scales.

To access the length scales—from 100 nm to 5 μm —associated with carbon-black agglomerates vanishingly small angles must be used. The BT-5 instrument at the NIST Center for Neutron Research uses neutrons to reach those length scales with the exquisite resolution of microradians.⁸ If human eyes had that resolution, we could read “United States of America” on a US penny a football field away. (Neutron experiments on the BT-5 are currently suspended as the NIST Center for Neutron Research conducts a repair, maintenance, and upgrade project scheduled for completion in 2026).

By performing neutron scattering on carbon-black suspensions subjected to well-defined flows in the rheometer, researchers were able to determine agglomerate size in the strong-flow region from the scattering intensity at different length scales. As seen in figure 3, a decrease in scattering intensity at the smallest inverse length scales demonstrates that agglomerates get smaller with increasing shear rates.^{9,10}

A series of experiments performed on samples containing varied types of carbon black, volume fractions, and suspending fluid properties were used to identify the role of those key formulation variables in determining the extent of agglomerate breakup.⁹ To summarize the full picture of factors affecting

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agglomerate size, researchers can use a dimensionless number known as the Mason number. It compares the volume-fraction dependent shear forces breaking agglomerates apart to the cohesive forces holding agglomerates together. The Mason number has been used in experimental work to predict the agglomerate size at a range of conditions⁹ (see figure 4), in agreement with computer simulations of similar systems.¹¹

The dimensionless Mason number can be computed with a few formulation variables to predict the size of the carbon-black agglomerates in suspensions. Work is currently underway to extend that framework to slurries that incorporate other solid particles and ingredients used to manufacture porous electrodes.

Revisiting slurries

Battery technology will continue to evolve. One aim of the industry is to reduce the reliance on cobalt as the active material ingredient because of geopolitical and ethical issues with its mining and availability.¹² Another is to incorporate higher-performance polymers. Unfurling the relationship between the formulation of carbon-black slurries and the structure of porous electrodes will remain a relevant problem well into the 21st century. It's unclear whether the Mason number will be able to universally predict the breakup of carbon-black agglomerates in more diverse battery systems that include different polymers and active materials. Further

quantifying that relationship will aid in the engineering and realization of defect-free coatings.

Manufacturers and academics alike need to understand how carbon black controls the complex rheology of its suspensions through the evolution of agglomerate microstructure. That research area remains ripe for both practitioners who seek to understand suspension formulation through quality control and academics who want to pull back the curtain on optically opaque suspensions.

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