

## TECH BEAT

Dr. Neil Canter / Contributing Editor

# Stretching salt

*A phenomenon known as superplasticity allows a material to stretch to more than 100% of its original length.*

## KEY CONCEPTS

- Salt on the macroscale is a brittle material that readily shatters like glass when placed under pressure.
- Salt exhibits superplasticity on the nanoscale as it can be stretched to more than 100% of its original length.
- Low levels of sodium metal present in the salt may act to keep the nanowires flexible and fluid-like.

**S**alt or sodium chloride is a typical ionic solid that we all know well from both personal and professional perspectives. This compound contains sodium and chlorine ions organized in face-centered cubic crystals. Electrostatic interactions between these ions are the source of the bonding that holds this compound together.

The presence of salt as a contaminant is a concern because it promotes metal corrosion. Salt is readily soluble in water and facilitates the movement of ions through metal, which accelerates the corrosion process.

Salt is also a brittle material that readily shatters like glass when placed under pressure. But when placed in a humid environment, salt becomes more ductile. Nathan Moore, postdoctoral researcher at Sandia National Laboratories in Albuquerque, N.M., says, "It is possible to bend and twist large pieces of salt as long as they are not just single crystals but are made of smaller grains."

Humidity facilitates the diffusion of atoms in the crystal, causing the salt structure to generate more defects such as steps, kinks and buried dislocations. This enables salt to exhibit bulk plasticity. Such a phenomenon is observed in large, underground rock salt deposits.

On the nanoscale, salt is organized into fewer ionic crystals or grains and so contains fewer defects, according to Moore. This means the likelihood is remote for salt to display any plasticity.

## SUPERPLASTICITY

Increasing demand for better quality water has spurred research efforts to develop more efficient desalination technologies. As part of this effort, Moore, in collaboration with other researchers, initiated work to better understand how water bonds to salt surfaces. He adds, "We were originally seeking to understand how salt and water interact on a molecular level in order to determine how to improve the ability to filter salt out of water."

In initial experiments, salt surfaces were studied under controlled humidity conditions using interfacial force microscopy. Freshly cleaved (100) crystal faces of 99.9% salt were evaluated in this study. Moore says, "Our intention was to prod the

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salt surface with a diamond tip in order to detect water.”

As the tip approached the salt surface, the researchers were surprised to encounter an unknown and unexpected force that did not fit any classical models. Once this force is established, the tip starts to pull salt from the crystal. Moore says, “We were very surprised to see salt become stretched into nanowires as it was pulled from the salt surface.”

This behavior is known as superplasticity, which Moore defines as the ability of a material to be stretched to more

surface.”

It is clear that this phenomenon involves the unexpected breakage of salt’s crystal structure. An attractive force is present between the probe and the salt surface. Moore says, “As the probe withdraws from the crystalline structure, a bubble or meniscus of salt is formed. When further stretched, the meniscus follows the tip and becomes elongated.”

In contrast, withdrawing an object from liquid water would form a meniscus that breaks under its own weight.

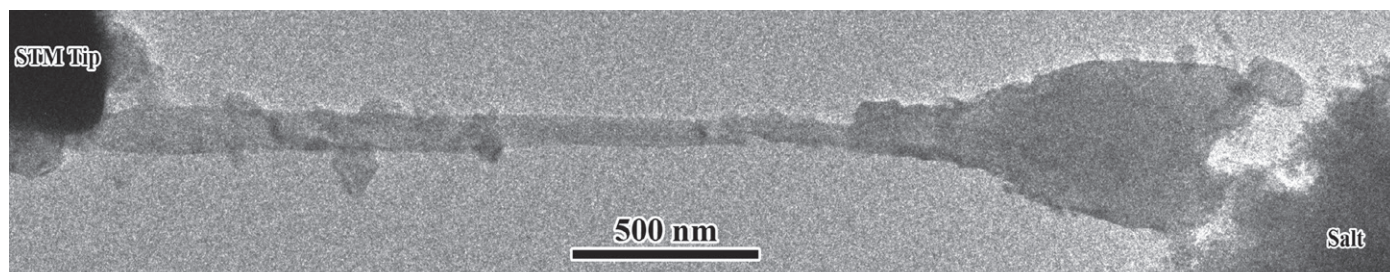


Figure 1 | Salt at the nanoscale can be stretched to more than 100% of its original length. This effect is known as superplasticity. [Courtesy of Sandia National Laboratories]

than 100% of its original length. Initial work was conducted at a relative humidity of 0.1% at ambient temperature. No change in the superplasticity of salt was seen as the humidity was raised up to 60%.

Further studies were conducted using transmission electron microscopy (TEM) under high-vacuum conditions. Moore says, “In this procedure, a 100 keV (kiloelectron volt) electron beam was operated at a dose rate of 1 ampere per square centimeter.”

A gold scanning tunneling microscope probe is pushed against the salt surface generating what the researchers consider to be “debris” in the shape of nanowires. Figure 1 shows salt stretched in this fashion over 2,000 nanometers.

Salt is hygroscopic, and Moore follows the general rule of thumb, “If salt is there, water is there.” But Moore believes the TEM experiments indicate that water does not contribute to the superplasticity. He says, “Under the conditions of the TEM work, the electron beam would blast most of the water away from the salt surface. A tiny bit of water may be present, but it is not believed to enhance the superplasticity effect.”

Salt was stretched up to a maximum of 2.2 microns, which represents an elongation effect of 280%. The researchers were limited by the range of the probe and could not stretch the salt further. Nanowire thickness is in the range of 210 nanometers, according to Moore. He adds, “When we are able to break the nanowire, it ruptures in the middle producing debris that comes close to the probe and to the salt

Salt is also acting as a fluid, but the meniscus produced just becomes extended without rupturing.

Use of the electron beam seems to enhance this effect. Moore explains, “The electron beam facilitates the reduction of a small fraction of the sodium cations to neutral sodium metal with the accompanying loss of chlorine anions. Sodium metal may stabilize the nanowire structure.”

Moore believes that sodium metal can provide stability to the salt nanowires as they stretch. This is accomplished because sodium metal gets in the way of sodium and chloride ions that would otherwise try to reform into a unified, rigid crystal. Thus, the small fraction of sodium metal may be one key to keeping the nanowires flexible and fluid-like. Nanowires have also been made completely out of sodium metal.

This research shows that the properties of salt can be very different at the macroscale compared to the nanoscale. Further work is needed to determine how salt nanowires may influence the corrosion process.

Additional information on this research can be found in a recent article<sup>1</sup> or by contacting Moore at [nwmoore@sandia.gov](mailto:nwmoore@sandia.gov). A video showing the salt nanowire being stretched has been posted on YouTube and may be accessed at the following link: <http://www.youtube.com/watch?v=OGcFCD8E7o8>.

### REFERENCE

1. Moore, N., Luo, J., Huang, J., Mao, S. and Houston, J. (2009), “Superplastic Nanowires Pulled From the Surface of Common Salt,” *Nano Letters*, **9** (6), pp. 2295-2299.

# Electronically controlling lubricant filtration

*This purification system enabled a fleet owner to extend operating intervals for trucks to 120,000 miles between oil changes.*

## KEY CONCEPTS

- A lubricant purification system that removes both solids and liquids has now been upgraded through electronic monitoring.
- This new system now constantly evaluates the condition of the lubricant and automatically adjusts the filtration and evaporation processing to maximize contaminant removal.
- Customers see a return on investment in less than a year with minimal maintenance.

**T**he continued tightening of heavy-duty diesel emissions has placed more maintenance pressure on fleet operators. Current EPA emissions standards in 2010 for particulate matter are now 0.01 grams per hp hour. NO<sub>x</sub> emissions cannot exceed 0.2 grams per hp hour.

Sulfur content of diesel fuel has been reduced from 500 ppm to 15 ppm. The latter is considered Ultra-Low Sulfur Diesel and will be required for all on-highway vehicles in December 2010.

Filtration is an important part of the process of maintaining automotive lubricants so they can perform at the levels required to provide good performance and minimize emissions. In a previous TLT article, a new type of filter based on nanofiber technology was discussed.<sup>1</sup> This filter provided an upgrade in efficiency due to its ability to operate on both the macroscopic and microscopic levels.

But solids are only a portion of the contaminants found in automotive lubricants. Liquid contaminants also are present, which means that an additional approach is needed to remove them as well.

A dual approach to removing contaminants can lead to a more efficient procedure for extending the operating life of the automotive lubricant. Optimization of this process through electronic control has not been available until now.

## ENHANCED FLUID PURIFICATION

Oil Purification Systems, Inc. (OPS), in Shelton, Conn., produces a unique technology that removes both solids and liquids from lubricants. Bill Priest, OPS' vice president of engineering, says, "Our approach is to remove solids and then liquids in a purification system that is maintained onboard the vehicle and used during its operation. The purification system is installed in a bypass configuration so as not to interfere with the engine filter."

The company has just developed a new product called Eco-Pur™ that electronically monitors the condition of the lubricant and automatically adjusts the filtration and evaporation processing to maximize contaminant removal. The new system is based on technology developed with the company's OPS-1 product and is an evolution of that system.

Priest says, "Our new approach utilizes state-of-the-art electronics to monitor and control performance, providing optimal efficiency regardless of environmental

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conditions. This product can be used in many more applications.”

The first step is to remove solid contaminants through filtration. Priest explains, “A proprietary microglass media is used to remove solids from lubricants. Our reinforced, pleated filters are designed to utilize the mechanisms of interception, sieving and bridging. This enables contaminants to be captured and retained over extended periods of time with minimal restriction in flow across the media.”

The filter has an efficiency of 94% in removing particles that are 3 microns in size and larger. Priest adds, “The filtration enables the 5- to 10-micron particles that are most likely to inflict wear on the engine to be removed.”

In the second step, the lubricant is moved into an evaporation unit to remove liquid contaminants. Priest says, “Our patented process for removing liquid contaminants from fluids includes a number of factors required for efficient evaporation. The technique starts in an evaporation chamber that utilizes laminar flow of the filtered effluent over a uniquely designed metal chamber known as a platen. The platen is heated to provide sufficient energy to the fluid to facilitate vaporization of the contaminants.”

Priest continues, “Once the vaporization is achieved, a pressure differential created in the evaporation chamber due to the temperature difference with ambient conditions creates sufficient flow to remove any vapor generated during the cleaning process.”

Priest indicates that the main contaminant removed in this fashion is water. No foreign component is added to the lubricant at this stage. The impact to the components and lubricant basestock is minimal. Priest says, “The emissions from our system have been tested by accredited testing facilities and found to be innocuous. There is also no direct impact on the lubricant basestocks or additives used.”

Priest maintains that the evaporation process subjects the fluid to much less energy than is found in the engine. He adds, “We have seen this from the thousands of samples analyzed with a myriad of lubricants.”

The evaporation process does not contribute additional detrimental emissions that could cause a commercial vehicle to violate current EPA regulations. Priest also indicates that the purification system is compatible with all lubricant base-

stocks, including synthetics such as polyalphaolefins, esters, polyalkylene glycols and phosphate esters.

The purification unit is very compact in size and only weighs 5 lbs. Priest cites this feature as a major benefit. He says, “Our approach is not dissimilar to that used in commercial dehydration systems with the primary difference being expediency. Lubricant flow through the unit is low, but we make up for this factor by being more efficient in terms of mass and volume.”

Most of the applications for the purification unit have been in automotive heavy-duty diesel engines. Priest says,

“Our technology has expanded to gear lubricants, hydraulic fluids, transmission fluids and even waste vegetable oil.”

This purification system has enabled fleet owners to extend operating intervals leading to reduced costs and emissions levels. In one case, a fleet owner extended the operating interval for its trucks to 120,000 miles between oil changes, leading to a 60% reduction in costs.

In general Priest estimates that customers see a return on investment in less than a year. Maintenance of the purification unit is minimal and involves just filter changes. Samples of the lubricant are pulled periodically and analyzed to ensure that contaminant levels are minimized.

This new product installed in a commercial engine is shown in Figure 2. Additional information about the filtration and evaporation purification process can be found in a recent patent<sup>2</sup> or by visiting [www.ops-1.com](http://www.ops-1.com).

### REFERENCES

1. Canter, N. (2006), “Nanofiber-Based Oil Filters for Diesel Engines,” *TLT*, **62** (6), pp. 19-21.
2. Whitmore, C., Gutierrez, J. and Gutierrez, J. (2007), “Method of and System for Fluid Purification,” U.S. Patent **7,244,353 B2**.



Figure 2 | A new technology installed onboard a vehicle has been developed that electronically monitors the condition of the lubricant and automatically adjusts processing to maximize contaminant removal. (Courtesy of Oil Purification Systems, Inc.)

# Measuring nanoparticles

*A new technique called induced grating allows accurate measurement of particles below 200 nanometers.*

## KEY CONCEPTS

- **Dynamic light scattering has difficulty measuring small nanoparticles with sizes of 20 nanometers or lower.**
- **A new technique known as induced grating has been developed that can measure different nanoparticle sizes with the same signal intensity.**
- **Induced grating achieves this result by taking advantage of the fact that smaller particles diffuse faster than larger particles.**

**T**he continuing interest in using nanoparticles to improve the performance of lubricants is leading to the development of some interesting technologies. For example, TLT highlighted a nanoparticle-based lubricant package that imparts both lubricant and extreme pressure characteristics to lubricant fluids and greases.<sup>1</sup> The nanoparticle contained molybdenum disulfide combined with canola oil.

A second technology focuses on the use of a dispersion of a potassium borate nanoparticle in a fatty ester.<sup>2</sup> This nanoparticle-based lubricant additive has shown promise in automotive and industrial lubricant applications.

One of the challenges in working in this area is to accurately determine the size of the nanoparticles and see how this affects performance. The current technology for nanoparticle measurement is dynamic light scattering (DLS). In this technique, light hits small particles and gets scattered in all directions (Rayleigh Scattering). Due to the fact that small particles in solutions are undergoing Brownian Motion, a time-dependent fluctuation in the scattering intensity is then recorded and computed to generate the particle size and distribution information.

Yanyin Yang, product specialist at Shimadzu Scientific Instruments, Inc., in Columbia, Md., says, “DLS suffers from a major disadvantage in that intensity of the scattered light is proportional to the sixth power of the particle diameter. This means that DLS has difficulty measuring small particles of 20 nanometers or even lower.”

Yang adds, “For large particles, the underlying assumption of Brownian motion in DLS does not apply since they tend to become sediment and sink to the bottom.”

Moreover, when the sample has a broad distribution or contains contaminants and agglomerates, DLS becomes ineffective in a way that signals from larger particles or contaminants and agglomerates can overwhelm those from targeted smaller particles due to the restriction of Rayleigh Scattering. High signal-to-noise ratio in this case cannot be realized.

A new test method is thus needed to address the issues of DLS and accurately measure the size and distribution of nanoparticles. Such a technique has not been available until now.

## INDUCED GRATING

Shimadzu has developed a new approach to the measurement of nanoparticles known as induced grating. This technique accurately measures the size and distribution of nanoparticles with much less sensitivity dependence on particle size than that with DLS and is now commercially available as the IG-1000 single nonparticle size analyzer.

Yang explains, “In this analyzer, an array of electrodes is immersed in a sample of dispersed nanoparticles. Upon applying AC voltage, particles will be drawn toward the electrode array because of dielectrophoresis. Some areas will have a higher density of particles while others will have a lower density of particles. Therefore a

**The induced grating approach enables particles of different sizes to be measured with relatively the same signal intensity.**

special density grating is formed. When light hits this grating, it gets diffracted. The diffracted light intensity and pattern are then recorded.”

Yang continues, “Once the voltage is turned off, the nanoparticles begin to diffuse away from the electrodes. Smaller particles will diffuse faster than larger particles. Hence the change in the diffracted light intensity and pattern is computed to generate the data of particle size and distribution.”

The correlation between diffracted light intensity and nanoparticle diffusion time is demonstrated in Figure 3 for sizes ranging from 5 to 100 nanometers. Note that the light intensity decay speed is a function of particle size.

Grating-based spectroscopy also is used in several analytical instruments that evaluate lubricant samples. Among the techniques are atomic absorption, inductively coupled plasma and ultraviolet-visible light spectroscopy.

The induced grating approach enables particles of different sizes to be measured with relatively the same signal intensity. As a result, the signal from a group of 1 nanometer particles is equivalent to a group of 100 nanometer particles given the same volume. On the other hand in the DLS technique, instead of 1:1, the ratio becomes 1 to 1 million, which means accurate measurement of 1 and 100 nanometer particles simultaneously cannot be realized.

Particle sizes below 200 nanometers can be accurately measured by this technique. Yang says, “We can determine the size down to 0.5 nanometers. On the high-end, particles up to 500 nanometers can be tolerated. Above that size, the particles diffuse too slowly and do not show up in the final data for the sample.”

This technique involves minimum sample preparation other than dilution to the appropriate concentration. In addition, the installation environment requires nothing but a standard laboratory environment. No vacuum and no liquid nitrogen are required. The instrument is very compact and weighs only 15 kilograms. Compared to other nanoparticle analytical tools such as TEM (Transmission Electron Microscopy), it offers the users more convenience, and much less time and labor are needed for sample preparation. The analysis results are comparable and have been justified in the single nanosize by TEM, according to Yang.

A key strength of the induced grating analysis technique is that effects of contaminants or agglomerates are minimized due to the greatly reduced single sensitivity on particle size. This also allows mixed samples to be accurately measured.

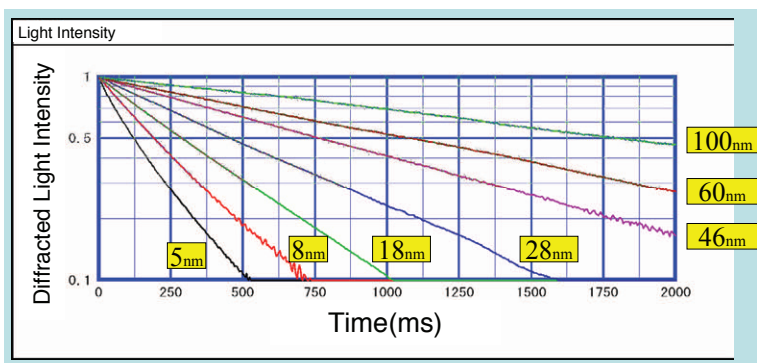


Figure 3 | The induced grating technique accurately measures the size and distribution of nanoparticles by taking advantage of the fact that nanoparticles of different sizes diffuse at different rates. As shown, the diffusion rate of 5 nanometer particles is faster than that of 100 nanometer particles. [Courtesy of Shimadzu Scientific Instruments, Inc.]

The use of dielectrophoresis means that metal nanoparticles may interfere with the electric field and cannot be measured. Yang provides an idea for circumventing this problem. She says, “The metal nanoparticles can be coated with an insulating layer that is compatible with the electric field. In addition, at the nanoscale, most metal particles are found to be oxidized already. For instance, important industrial nanoparticles made of metal oxides like titanium oxide and zinc oxide can be measured by induced grating without any problem.”

Another concern is that nonpolar solvents may not be used mainly because dielectrophoresis force is proportional to the dielectric permittivity. Nonpolar solvents have low dielectric permittivity leading to weak dielectrophoresis forces. In addition, the sample cell is made of Pyrex glass, which needs to be considered when choosing the solvent.

Yang comments, “We suggest that samples only compatible with Pyrex glass and solvents of relatively high dielectric permittivity be analyzed by the induced grating technique. Future work will involve evaluation of the possibility of using blended nonpolar and polar solvents using the induced grating technique.”

This method marks a step forward in the evaluation of nanoparticle size in a standard lab setting with minimum work spent on installation and maintenance.

Further information can be found in a recent article in *American Laboratory*<sup>3</sup> or by contacting Yang at [yayang@shimadzu.com](mailto:yayang@shimadzu.com). **TLT**

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1. Canter, N. (2009), “EP Nanoparticles-Based Lubricant Package,” *TLT*, **65** (4), pp. 12-13.
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Neil Canter heads his own consulting company, Chemical Solutions, in Willow Grove, Pa. Ideas for Tech Beat items can be sent to him at [neilcanter@comcast.net](mailto:neilcanter@comcast.net).