

Nanophosphate® Basics: An Overview of the Structure, Properties and Benefits of A123 Systems' Proprietary Lithium Ion Battery Technology

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Abstract

The overall performance and reliability of an advanced battery system depends largely on the chemistry used in the cell. Lithium ion, for example, is deployed in electric vehicles, grid-scale energy storage systems and a wide variety of commercial and industrial applications.

There are a number of different lithium ion chemistries commercially available today, however, each with distinct behavioral characteristics. Understanding the differences in these chemistries can prove invaluable in determining which battery system is best suited for a given application.

This paper outlines the unique properties of Nanophosphate®, a nanoscale lithium ion technology offered exclusively by A123 Systems, and how it differs from standard lithium iron phosphate as well as other lithium ion technologies. It also describes the resulting performance advantages, including high power, excellent abuse tolerance, long life and the ability to maintain consistent power over a wide range of state-of-charge (SOC).

History of Nanophosphate

Nanophosphate is A123 Systems' patented lithium ion battery cathode active material, originally developed by professor Yet-Ming Chiang and his group at the Massachusetts Institute of Technology (M.I.T.). They reported their work in the seminal paper entitled, "Electronically conductive phosphor-olivines as lithium storage electrodes," which was published in the journal *Nature Materials* in the [October 2002 issue](#) (Chung, Bloking, & Chiang, 2002).

In this paper, Professor Chiang and his group discussed the development of a unique new material belonging to a class of materials called the "olivines" based on their crystal structure. This new material exhibited dramatically higher conductivity and rate capability than standard lithium iron

phosphate materials, with near-theoretical energy density.

On March 4, 2008, the U.S. Patent Office granted U.S. Patent Number [7,338,734](#), titled "Conductive Lithium Storage Electrode" (Chiang, Chung, Bloking, & Andersson, 2002). This patent covers the Nanophosphate materials used in A123's products. The Nanophosphate material is patented worldwide and is not offered by any other battery manufacturer. Specifically, Nanophosphate should not be confused with standard lithium iron phosphate (LFP), which is has lower rate capability and power.

The Structure of Nanophosphate

Nanophosphate is an engineered nanoscale material with specific structural and chemical properties designed to maximize the performance of lithium-ion batteries. Figure 1 schematically illustrates this structure. The image on the left is a cathode electrode, with the aluminum current collector foil covered with Nanophosphate particles. The middle image is the Nanophosphate secondary particle and the image on the right illustrates the primary particles.

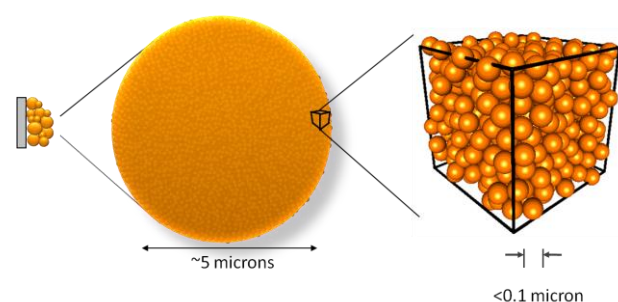


Fig. 1: Schematic illustration of the Nanophosphate structure, with secondary and primary particles

The primary Nanophosphate particles are on the order of one-tenth of a micron in diameter and are agglomerated into much larger secondary particles, which have diameters on the order of a few microns. So, although the primary particle may have a length scale on the order of several tens of nanometers, the

secondary particle is on the length scale of microns, making it well above the Environmental Protection Agency (EPA) definition of what is considered a nanomaterial. Micron-sized secondary particles allow the Nanophosphate powder to be handled and processed more easily.

This unique electrochemical structure of Nanophosphate enables a number of performance advantages, including higher power, excellent safety, long life and greater usable energy.

Power

Typical lithium-ion batteries store energy via a reaction between lithium ions and the cathode and anode material. The lithium ions are inserted or removed in active materials through a process called “intercalation.” However, these chemical reactions are generally slow, limiting the rate capability, or power output, of the battery. Thus, traditional lithium-ion batteries have high energy, but low power.

Conversely, the chemical reactions created in the Nanophosphate technology increase the cathode surface area with the electrolyte, which allows for faster lithium insertion and thus more power. At the same time, however, all of the bulk volume is still used to store energy, like other battery materials (as illustrated in Figure 2).

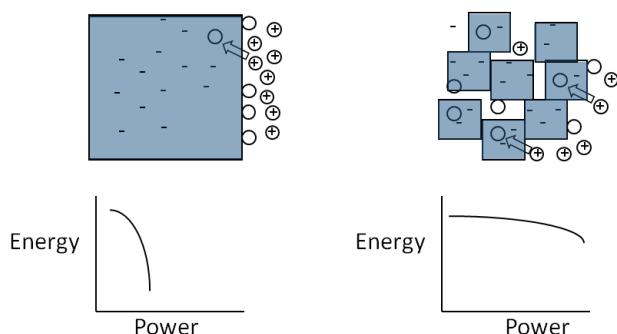


Fig. 2: Chemical reaction and energy/power balance of standard battery vs. A123 Nanophosphate

Another significant feature of the Nanophosphate technology is the consistent power capability over a wide range of states-of-charge (SOC). Most battery technologies have significantly lower power capability at low SOC. A123’s Nanophosphate retains its power capability at low SOC, widening the range where the applications’ power

requirements can be met. This also enables higher usable energy.

Safety

Battery safety is a critical requirement for most applications, and like other forms of phosphate-based cathode materials, Nanophosphate has excellent abuse properties. In these chemistries, all of the lithium ions are transferred during a complete charge/discharge event. In the case of most metal oxide cathode materials, including cobalt and nickel-based materials, only half of the available lithium is transferred during normal operation. When those metal oxide cells are overcharged, the excess lithium from the cathode cannot be inserted into the anode, which is already completely full. The result is that the lithium plates onto the surface of the anode, creating a hazard since metallic lithium is much more reactive than ionic lithium. Since all of the lithium ions in the Nanophosphate chemistry are transferred to the anode during charging, it is much less likely for lithium metal to plate onto the anode surface during an overcharge event.

Another significant advantage of Nanophosphate as compared to metal oxide cathodes is that it is much more stable chemically. When subjected to abusive conditions, such as high temperature or over voltage, metal oxide cathode materials can degrade, which produces an exothermic or heat-generating reaction that releases gaseous oxygen. This heat and oxygen combine with flammable electrolyte, and can support oxidation or combustion within the cell.

Conversely, Nanophosphate releases only a small amount of heat and oxygen under similar abusive conditions and cells made using Nanophosphate chemistry do not exhibit the energetic thermal runaway that metal oxide lithium ion cells experience (Roth, 2007). This greatly reduces the likelihood of cascading failure—where an incident in one cell spreads to adjacent cells—within a battery pack designed with Nanophosphate chemistry. Even if all of a pack’s safety systems fail, the increased safety inherent to Nanophosphate chemistry provides an additional layer of protection that reduces the incidence, severity and probability of energetic failures. Heavy and costly cooling and controls systems are used to mitigate the likelihood of thermal runaway in metal oxide battery designs, but these do not address the root cause of chemical instability.

Life

Both cycle life and calendar life are key metrics for advanced battery performance, especially for automotive applications. Cycle life is typically defined as the number of times a battery can be charged and discharged before its capacity falls below 70 to 80 percent of its original capacity or nameplate energy. Similarly, calendar or shelf life is defined as the ability of a battery to maintain discharge and regeneration energy over time, irrespective of use conditions.

Cycle life and calendar life are key metrics for any energy storage technology, because they affect the overall usability, total cost of ownership and return on investment in the technology over time.

To fully understand battery degradation, it is important to examine power and energy and how they change over time. A common way to measure this is to plot capacity or energy as a function of number of cycles. This shows the gradual degradation of the battery in use. A battery is generally considered to have reached the end of life when it loses 20 percent of its capacity or energy.

Nanophosphate technology performs better than competing chemistries on cycle life testing. As illustrated in

Fig, batteries designed using Nanophosphate deliver more than 7,000 cycles when charged and discharged at a one-hour (1C/1C) rate and 100-percent depth-of-discharge (DOD) with little impedance growth or power loss. The energy retention is also very high.

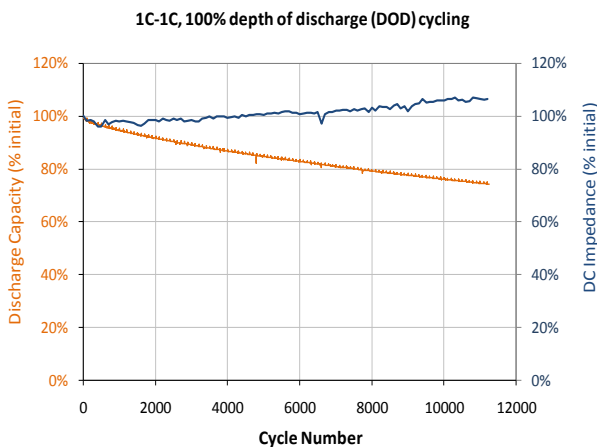


Fig. 3: 1C-1C, 100% DOD cycling of 26650 cell, showing capacity and impedance as a function of cycling

A123's 20Ah prismatic cell shows similar cycle life (as show in Figure 4). When subjected to calendar life tests at elevated temperatures, the prismatic cells are projected to have a lifespan of 15 years or longer in automotive applications.

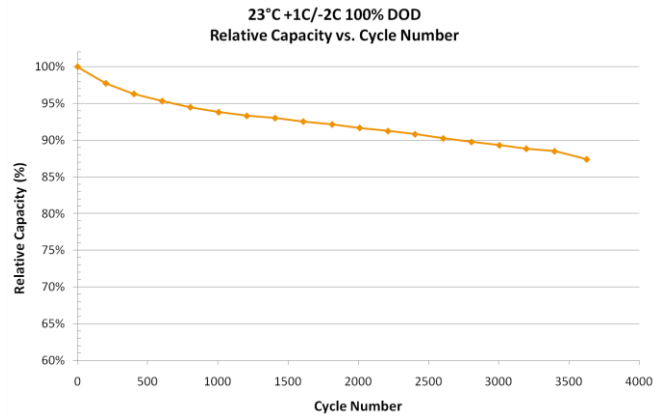


Fig. 4: 1C-2C, 100% DOD cycling of 20Ah prismatic cell, showing capacity as a function of cycling

Increased cycle and calendar life translate directly to a lower total cost of ownership of Nanophosphate cells as compared with traditional batteries by allowing the battery pack to be “right-sized” to an application. Traditional battery chemistries require packs to be oversized so that as the cells degrade and lose power, they still meet performance requirements at the end of use. This adds considerable initial cost and causes a significant excess in the application’s power needs at the beginning of use. In other words, the pack must be much larger and more expensive because it will degrade significantly in usage. The Nanophosphate technology retains its energy and power better than many competing technologies, which means that a pack using Nanophosphate technology need not be oversized as much. In most applications, this translates to a smaller, less expensive pack.

Usable Energy

Although some lithium ion battery makers cite high specific energy (measured in Wh/kg) as their key advantage, not all of the stored energy in those products is usable under real-world automotive conditions. The more meaningful metric is usable specific energy, which is the Wh/kg available over the useful SOC range of a particular cell chemistry.

For example, some manufacturers may limit the maximum and minimum voltage, thus reducing the voltage window where the battery may operate and limiting the system's usable energy. This is typically done for one of three reasons.

First, lowering the maximum SOC can improve the abuse tolerance or safety of the system. Fully charged batteries are more energetic than partially charged batteries, so by only partially charging the battery, the severity of the reaction during a catastrophic abuse event is reduced.

Second, lowering the maximum SOC improves the life of the battery, both with respect to cycle and calendar life. In cycle life, reducing the maximum SOC reduces DOD. This means that the battery is cycled more shallowly, which causes less degradation. At the same time, batteries in the fully charged state have more oxidative side reactions which can cause the cell to lower capacity and power.

The third reason why the SOC window may be narrowed is to preserve a consistent power capability from the battery. Most lithium ion battery technologies lose a significant amount of discharge power at low SOC. In order to ensure that the battery meets minimum performance requirements, it is restricted from reaching a low SOC.

Nanophosphate technology, on the other hand, has excellent abuse tolerance and life, which allow it to be charged to full SOC with minimal impact on life. In addition, the power capability is excellent at low SOC, allowing the battery to more fully use the operating window. These factors increase the SOC window and in turn, the amount of usable energy that is available (as illustrated in Figure 5).

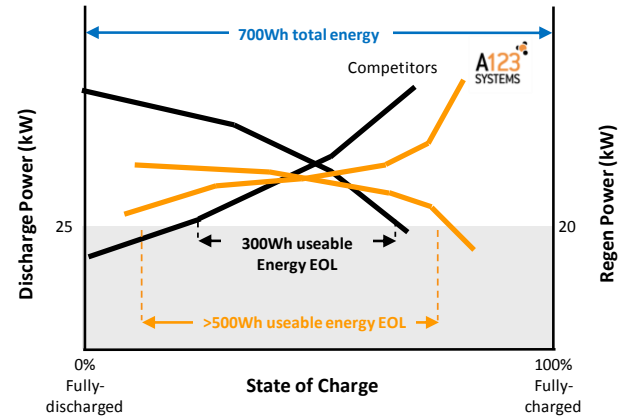


Fig. 5: Power output of A123 and leading competitor over a wide range of state of charge (SOC)

Conclusion

As the markets for electric vehicles and grid-scale energy storage systems grow, understanding the performance benefits associated with each battery chemistry's distinct characteristics will become increasingly important.

Lithium ion is quickly emerging as the optimal battery chemistry for transportation, electric grid and commercial applications, but not all lithium ion technologies behave the same.

The nanoscale structure of the Nanophosphate chemistry, for example, enables battery systems with higher power, increased abuse tolerance, longer life and the greater ability to maintain consistent power over a wide range of state-of-charge (SOC) as compared with competing lithium ion and other chemistries.

Understanding the fundamental chemical differences between Nanophosphate and other technologies is necessary to develop a complete and accurate assessment of the optimal advanced battery system that will deliver the best performance for a given application.

References

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