by Tom Keim

New Uses Spur Lithium-Ion Battery Research and Development

Driven in part by increased interest in electrification of land transportation and by the increased use of wind- and solar-generated electricity, lithium (Li)-ion battery research and development (R&D) is exploring many innovations. This article discusses potential new directions in the Li-ion battery industry. It starts with a few paragraphs about the basics of the technology and the evolution of the product line and then offers a discussion of future directions.

Both electrodes in a Li-ion battery are complex structures consisting of active materials, binders, and current collectors. In both electrodes, the active materials have a crystal structure that comprises pronounced layers. Today, the active materials are one of several complex metal oxides for the cathode and graphite for the anode. The Li is stored between layers in both electrodes. As the battery charges and discharges, Li ions are cycled back and forth between the electrodes and physically move from one electrode to the other. The cathode is the positive terminal, and the anode is the negative terminal.

There are a number of different chemical formulations for the metal–oxide cathodes, which enable the design of batteries with usefully different properties. Further discussion of these differences is not within the scope of this article.

The first commercial Li-ion battery was introduced by Sony in 1991. Early applications included cell phones, laptop computers, and some camcorders. In these applications, the high specific energy, combined with the low self-discharge rate, and acceptable cycle life were primary attractions. The target products had moderate expected product life, and battery replacement, while undesirable, was not unthinkable. Wikipedia reports that, by 2012, approximately 660 million cylindrical Li-ion batteries were produced. Most of these were 18650 cells, so named because they are nominally 18 mm in diameter and 65 mm long. For many years, 18650 cells were the mainstay of the laptop market, but by 2012, that industry was migrating to thinner form factors, which could not accommodate the 18-mm diameter. Today, 18650 cells are still produced in great quantity. The Tesla Model S and Model X battery-electric automobiles use battery packs built up of thousands of these cells, connected both in series and in parallel to produce the desired battery capacity and voltage.

Dr. Brian Barnett is a longtime industry contributor and observer. Over his career, he has worked for and led major battery activities at Arthur D. Little, Tiax, and CAMX Power LLC. Most recently, he has established a small consultancy, Battery Perspectives LLC. Dr. Barnett reports that, today, few (if any) new laptop computers use cylindrical cells; instead, they are built with thin flexible rectangular cells called *pouch cells*. Dr. Barnett attributes the continued production of 18650 cells to other applications, including the aforementioned Tesla models and probably many rechargeable electric power tools. Other, smaller consumer markets have adopted the 18650 cell, including some e-cigarettes.

In addition to cylindrical cells and pouch cells, other cells are produced with generally rectangular rigid cases. Many automotive battery packs are made up of such cells.

Dr. Barnett points out that a modern 18650 cell can deliver about three times the energy of an early production cell (approximately 3.5 Ah, or about 13 Wh). Also, the power available from such a cell has increased substantially more than a factor of ten over the same period. Some of these advances reflect a reduction in conservatism, justified by accumulated experience. But much of the difference is attributable to advances both in materials and in cell design.

According to Dr. Barnett, further improvement, relying principally on improved cell design with existing or similar materials, is approaching a ceiling. The technical community believes that the next jump in energy density will be achieved by more fundamental changes. For this reason, R&D in Li-ion battery technology is, if

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anything, more robust than in the past. Certainly, both the electrification of transportation and the conversion to intermittent renewable generation of utility power are large potential markets, which may be enabled or accelerated by continued advance in battery capability. Furthermore, even low estimates of the future demand for batteries for vehicles will require more than a doubling of the production rate for batteries, and storage for the power grid, when it comes, will be a larger market still.

The U.S. Department of Energy Vehicle Technologies Office issued a progress report on Department of Energy-funded battery R&D for 2016 that exceeds 1,000 pages. Looking at the index, it is evident that there are many battery technologies under investigation, not only Li-ion batteries. But it appears that substantially more than half the report is devoted to Li-ion technology. The report for 2017 is even longer. Much additional work is funded from other sources, including investment in start-up companies.

While there are already a large number of different formulations for cathode materials on the market, more are being developed. Dr. Barnett is included among the authors of a recent paper "High-Nickel Cathode/Graphite Anode Cells for Diverse DOD Applications." This paper was presented in June 2018 at a long-running conference series for developers of power supplies for military uses [1]. The high-nickel cathode material that is the subject of the paper was developed and patented by CAMX Power and licensed for commercial production by global battery materials companies. The paper compares cells with this cathode material to cells with other common materials, on the basis of specific energy, energy density, and specific discharge capacity. The differences are mostly small, but in every comparison, the new cathode is superior.

There is also a substantial ongoing body of work attempting to develop higher-performance anodes. Unlike cathode technology, where different active materials are preferred for different uses, almost all commercially produced cells today use very similar technology based on graphite. The layered structure of graphite accommodates the storage of Li when the cell is in the charged state and the release of ions to travel to the cathode during the discharge cycle. Much of the current work is directed to substituting silicon for graphite. The potential is huge. It takes six carbon atoms to accommodate one Li atom, whereas one silicon atom can accommodate four Li atoms.

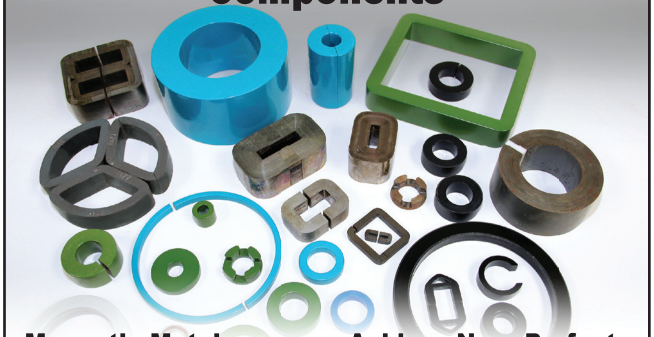
But in absorbing that much Li, a silicon structure grows in volume by a factor of more than three. Few materials can undergo such a large volume

change reversibly, and bulk silicon is not among them. Today, there are a number of start-up companies pursuing a way forward to use silicon in anodes. One of these is Amprius Corporation. The company is working to commercialize a process developed by Prof. Yi Cui at Stanford University, California, whereby silicon nanowires are used to provide host sites for the Li while providing the flexibility to accommodate the volume change without destruction. The company has encouraging results and substantial funding but does not appear to have made any major announcements in recent years.

An apparently balanced assessment appeared in the magazine *Joule* in 2017. A group of authors from the Ulsan National Institute of Technology in South Korea presented a perspective article, “Confronting Issues of the Practical Implementation of Si Anode in High-Energy Lithium-Ion Batteries.” The article discusses the reasons why silicon offers potential. It also indicates that there are a number of ongoing problems that need to be resolved before the technology’s potential is realized. This work has been ongoing for 20 years. Yes, things are happening in silicon anode research, but the technical progress is not currently disrupting the market.

The modern Li-ion battery was, to a large degree, made possible by the development of graphite-based anodes. Much of the previous research focused on metallic Li for the anode. Li metal is an excellent source of Li ions, but cycle life and safety proved to be problems. When graphite-based anodes were developed, interest in using metallic Li diminished substantially. Nevertheless, the search for improved anode materials is leading to renewed interest in developing metallic Li anodes, even as most developers acknowledge that more work needs to be done before such systems can be brought to commercial fruition.

Efforts continue to make Li-ion batteries safer. The principal safety issue is that mechanical damage, external overheating, or malfunction in normal service can cause a thermal runaway event. This possibility requires attention during system design to limit the consequences of such events to acceptable levels and to reduce the resulting ongoing costs to produce safe systems. Malfunction in normal service is controlled principally by adequate quality control during the production of the cells. It is possible to produce cells in great quantity without malfunctions in normal service. But as long as the possibility of thermal runaway due to other causes remains, safety will be an important issue.



Thermal runaway events can arise in several fundamentally different ways. An internally grown short circuit is typically the result of an impurity introduced during manufacture. But the other causes of thermal runaway can be attributed to a range of events, almost all of which can be characterized as cell abuse. Safety against thermal runaway is thus highly correlated with abuse tolerance.

Long-term overcharging is one example of a condition that can give rise to thermal runaway. But even if a cell is removed from the circuit, exposure to a moderately hot environment can cause a problem, as can mechanical abuse of the cell, e.g., by crushing or puncture. The detailed description of the steps in the process of failure varies significantly among these alternatives, as does the range of precautions against them. But the end result is often similar.

Much is made of the possibility of the internal conversion of the stored electrochemical energy to heat. This is significant, but it is far from the whole story. There are a number of complex chemicals in a cell, and they begin exothermic thermal decomposition at temperatures as low as 80–100 °C. More significantly, the electrolyte is a combustible substance with a specific heat of combustion not that far below petroleum-based fuels.

The total available heat of combustion can be several times the electrochemically stored energy. If the event is initiated by a rupture of the cell, it is common for the electrolyte to burn, substantially contributing to the overall event. Even if the cell is not ruptured at the onset, internal heating can result in pressurization of the contents, which can result in a flame-thrower event should the cell fail under pressure. There is ongoing work on alternative electrolytes that are not flammable, but currently none have had a combination of properties that has resulted in displacement of the incumbent materials.

It is common for a thermal runaway result in one cell to start the process in nearby cells in a battery pack, often resulting in the failure of a second cell after a delay of seconds or even minutes. It is possible for a cascading failure to result in loss of the entire battery pack.

Another interesting development may have positive implications for the safety of future batteries. Ionic Materials, a Massachusetts start-up company with ties to Tufts University, has developed useful quantities of a solid polymeric material that replaces both the electrolyte and the separator in an otherwise conventional battery. The material is far less flammable than present electrolytes and is claimed to allow the passage of Li ions as well as a conventional electrolyte does.

This development is the subject of an impressive segment in an episode of the long-running PBS television show *Nova* [2]. It is almost irresponsible to recommend it, because it contains egregious violations of standard laboratory safety precautions, but the results are too impressive to ignore. What is clear is that prototypes of pouch cells the size of a digital tablet device are extremely resistant to thermal runaway due to puncture by metal objects.

Conspicuously absent from the discussion, and also from the company website, are any claims that cells with the new material have been built that are competitive with conventional cells on the basis of specific energy or any of the many other properties on which batteries are judged.

Even farther from being proven, at least in public, is the assertion that the new solid electrolyte will allow the use of a metallic Li anode. It is widely accepted that if Li metal can be used, the specific energy of batteries could be substantially advanced, probably rendering both graphite and silicon anodes obsolete. Ionic Materials claims that specific energy can be doubled by such a substitution. There are historical reasons to be cautious about the safety of a metallic Li anode and other reasons to question whether such a large increase in energy per unit mass would be achievable. But a safe doubling of specific energy would likely be a major market success if it were to be achieved.

It is apparent from credible public sources that Ionic Materials, like Amprius, is a serious company, with serious investors and capable employees, working on an important problem. It appears that the company currently has enough funding and that it is visible and well connected enough to have access to more if progress warrants it.

Likewise, it has been established that Li-ion research is being conducted on innovative anodes and cathodes, and literally on everything in between. The industry is strong and growing, and it is reasonable to expect that changes in the capabilities of Li-ion batteries will continue.

About the Author

Tom Keim (tkeim@alum.mit.edu) is a late-career engineer and a longtime Member of the IEEE. His specialty is high-performance electromechanical systems and the power systems that drive and control them. He has worked for a worldwide conglomerate, for a small (50 employees) innovative research and development company, for a major research university, and for an engineering consulting company. He has 50 publications and 11 patents and is currently active as an author, inventor, and consultant.

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