



Solid-state electrolyte batteries are lightweight, reliable, recyclable, safe and, as the juxtaposition with the keyboard shows, small.

(Credit: Planar Energy.)

 bulletin | cover story

The state of solid-state batteries

by Kevin S. Jones, Nicholas G. Rudawski, Isaiah Oladeji, Roland Pitts, Richard Fox

Solid-state batteries offer a promising future for energy storage applications.

Providing sufficient energy for the world's population is the grand challenge of this century. An integral part of that challenge is to provide energy storage for the full range of human activity, so that energy use can be efficient. Chemical energy storage in the form of batteries will contribute strongly to the energy storage picture, from powering sensors to personal mobility devices, transportation and even some grid storage applications. We as a society are becoming increasingly dependent on batteries. For example, with the recent interest in decreasing greenhouse gas emissions and dependency on foreign oil, there is an increasing interest in better batteries for high-range electric vehicles. Much of the

population has smart phones and every night we race home to charge them up because the batteries have limited capacity. Batteries vary dramatically in size from microbatteries with energy capacities of milliwatt-hours to grid storage batteries with capacities of megawatt-hours. The challenge is, how do we increase the charge storage capacity of all these batteries safely and economically?

Lithium-ion battery technology¹ has the highest specific energy and energy density of any known battery chemistry, and, therefore, the market forecasts for LIBs look very promising (Figure 1). However, LIB technology faces many challenges in terms safety, cost, cycle life and optimized energy density. Many of these challenges are associated with the use of a highly reactive liquid electrolyte.

To address these challenges, an alternative to the typical liquid-based LIBs has been actively pursued during the past 20 years. This alternative uses a solid-state electrolyte and, thus, is termed a solid-state or thin-film battery. Although still in its infancy relative to liquid-based batteries, recent developments and continued interest indicate a promising future for solid-state batteries for many energy storage applications.

Lithium-ion battery structure imposes limitations

To understand the challenges faced by liquid-based LIB technology, it is necessary to understand

the structure of a battery. A battery typically consists of three main components: the anode (negative electrode), the electrolyte; and the cathode (positive electrode).

During discharge, lithium ions migrate through the liquid electrolyte from the anode to the cathode. A polymer separator electrically isolates the cathode from the anode.¹ The liquid electrolyte is typically LiPF_6 dissolved in a mixture of organic solvents (e.g., dimethyl carbonate, diethyl carbonate, ethylene carbonate).³ The performance of the battery is, in part, determined by the performance of the electrolyte.

Specifically, it is desirable for the electrolyte to have a very high ionic conductivity to facilitate rapid shuttling of lithium ions between the electrodes to maximize power delivery, while having very low electrical conductivity to limit self-discharge and prolong self-life. Additionally, the ability of the electrolyte to perform effectively over a wide temperature range is crucial for many applications. Liquid electrolytes meet all of these criteria, having typical ionic conductivities on the order of approximately 10^{-3} siemens per centimeter, extremely high electrical resistivity and effective operating temperatures from a few tens of degrees below 0°C to approximately 100°C .³

However, there are serious safety concerns regarding the use of liquid electrolytes. The use of organic-based solvents often makes liquid electrolytes highly volatile under extreme operating conditions (high temperatures, high charge-discharge rates, puncturing, etc). This in turn leads to safety concerns about battery flammability in everything from personal mobility devices to electric vehicles.

Another key aspect of battery operation is the amount of lithium that can be stored in the electrodes. The more lithium the electrodes can store and release, the higher the capacity and the more energy that can be extracted during operation. However, the liquid electrolyte can react with the surfaces of the cathode and anode, forming a solid-electrolyte interfacial layer,⁴ which can protect the electrode but also adversely

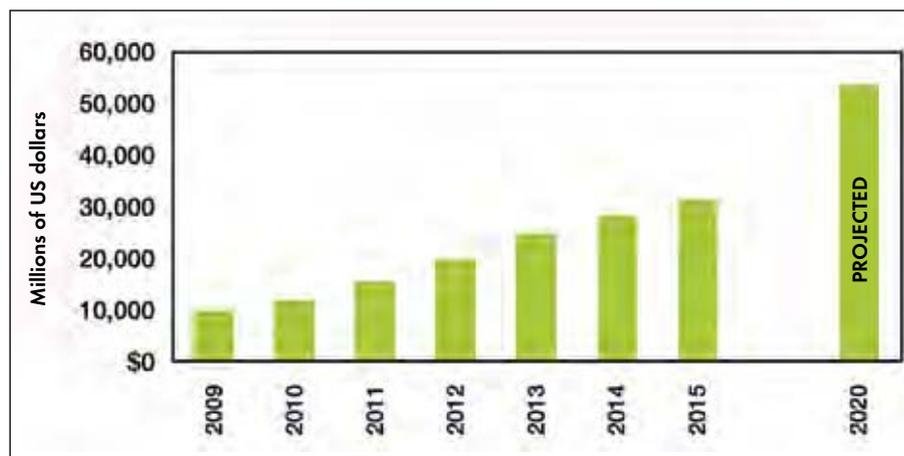


Figure 1 Global lithium-ion battery revenue is expected to exceed \$50 billion by 2020, driven in large part by the electric vehicle market.¹ Estimated present solid-state battery sales are less than 1 percent of LIB market. Source: IHS iSuppli, August 2011.

affect electrode performance by increasing resistance to charge flow during cycling.

This can lead to fading of the battery, which means the capacity of the battery drops as the number of charge and discharge cycles increases. Decreased cycle life with continued use is a common occurrence and often seen in cell phone and laptop computer batteries. These secondary reactions can also lead to decreased battery life with increasing temperatures.

In addition to the active electrode materials in the battery, there also are a number of additives, such as carbon and binders, that enhance electronic conduction and hold the materials together during fabrication. These not only add weight and volume to the cell but present additional surfaces to the electrolyte where unwanted reactions occur, limiting battery performance and lifetime.

Cathodes for currently commercially available LIBs consist of intercalation materials,⁵ such as LiCoO_2 , LiMn_2O_4 and LiFePO_4 . The most common cathode is LiMn_2O_4 , which has a spinel structure, versus LiMnO_2 , which is a layered structure compound. The intercalation process involves the insertion and storage of the lithium into the interstitial sites in the cathode without altering the crystal structure of the material. The specific capacities of these materials are generally limited to below 200 milliamp-hour per gram.

The anode most commonly used is graphite, which has a specific capacity of 372 milliamp-hours per gram, where,

again, intercalation is used to store the lithium upon recharging of the battery. The potential difference between the lithium in the graphite and the lithium in the cathode determines the voltage of the battery, and this in turn affects the total energy the battery can store.

To get the most power and energy from a battery, it is desirable to operate at the highest voltages possible. However, because of the inherent instability of liquid electrolytes, using certain electrode materials to produce higher battery voltages is challenging.

Solid-state electrolyte development

To help circumvent these issues, there has been an interest for many years in developing a battery that uses a solid-state electrolyte. During the initial development of viable SSEs, it was evident that the main challenges would be preparing a solid-state material with sufficiently high lithium-ion conductivity, sufficiently high electrical resistivity, favorable temperature stability and good stability in contact with typical LIB electrodes. Figure 2 shows a schematic comparison of liquid electrolyte LIBs and thin-film SSE batteries.

Early work⁶ revealed LiN_3 to have ionic conductivity comparable with liquid electrolytes, but the electrical resistivity was too low to prove viable as an effective SSE. Researchers also investigated several lithium-ion-conducting compounds, including lithium phosphosilicate glasses,⁷ lithium chalcogenide glasses^{8,9} and glass-ceramic compounds.¹⁰ Some of these materials

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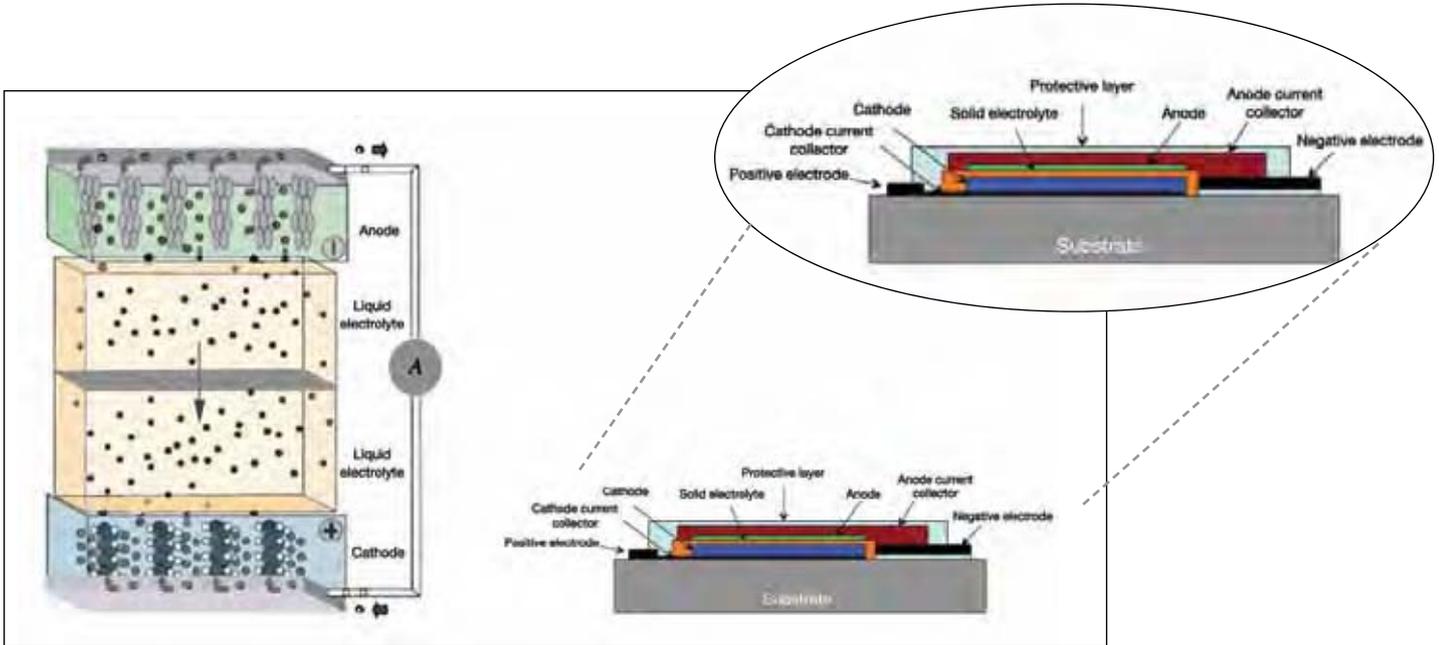


Figure 2 Side-by-side comparison of liquid electrolyte lithium-ion batteries and thin-film solid-state electrolyte batteries.

exhibited ionic conductivities comparable with liquid electrolytes but suffered from excessively low electrical resistivity, poor temperature stability or poor LIB electrode stability.

It was in the 1990s that workers at Oak Ridge National Laboratory produced a new class of SSEs via the introduction of nitrogen into Li_3PO_4 to produce lithium phosphorus oxynitride.¹¹ The highest reported ionic conductivity of LIPON is approximately 2×10^{-6} siemens per centimeter, which is about three orders of magnitude lower

than that of typical liquid electrolytes.³ However, LIPON was revealed to have very high electrical resistivity, good temperature stability, and excellent stability in contact with metallic lithium and other electrode materials.¹² Furthermore, LIPON proved viable for use as a SSE in thin-film-lithium metal batteries because it allows the electrolyte layer to be less than 2 micrometers thick (which minimizes the influence of the relatively low ionic conductivity).^{13,14}

Subsequent to the discovery of

LIPON, several companies began developing thin-film solid-state microbatteries.¹⁵ Presently, there are at least seven companies selling commercial solid-state or thin-film batteries based on thin-film technology. The market for these batteries, as illustrated in Figure 3, is typically in the area of powering sensors, RFID chips, medical devices, on-chip battery back-up and even energy storage from energy harvesting devices, such as photovoltaics and piezoelectrics.

The typical length and thickness of these prismatic batteries is 2–6 centimeters and 1 millimeter, respectively, which facilitates flexibility and allows for potential application in wearable electronics. The areal energy storage capacity of these batteries is typically 0.02–0.15 milliamp-hours per square centimeter with total capacities of 1–2 milliamp-hours. (For reference, a typical cell phone battery has a total capacity of approximately 1 amp-hour, an amount about three orders of magnitude greater than that of typical thin-film solid-state batteries.)

Small size, big advantages

Despite the small size, there are many advantages to solid-state batteries compared with a battery using a liquid electrolyte. Because solid-state batteries contain no flammable material and cannot produce hydrogen gas

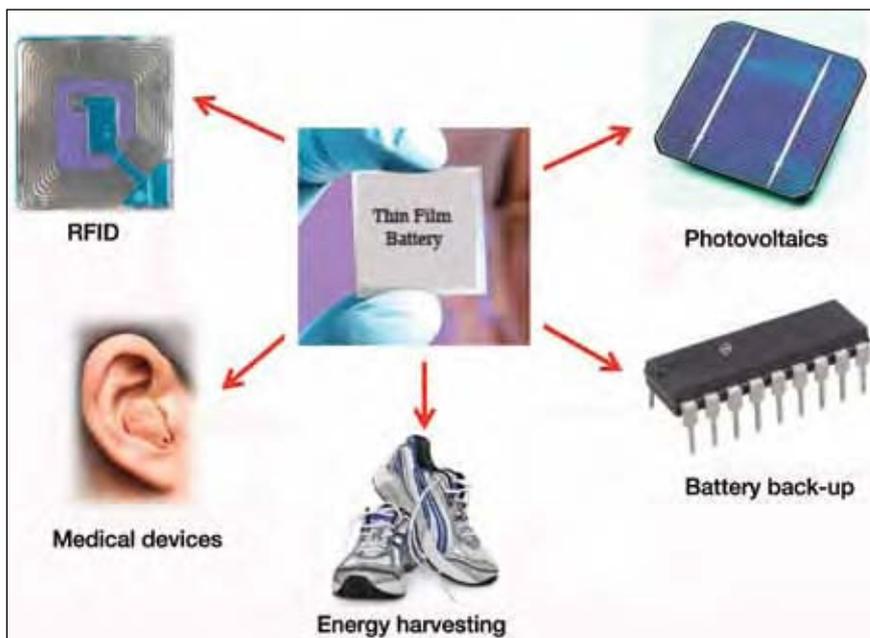


Figure 3 Applications for thin-film solid-state batteries.

Liquid cell	Solid-state cell
Inexpensive processing	Expensive processing
Large format in production	Only small format in production
Flexible separator accommodates some mechanical stress	Ceramic separator. Rigid, may break with mechanical stress
Low interfacial impedance	Interfacial impedance can be a problem
Higher ionic conductivity near room temperature	High ionic conductivity over broader temperature range
High electrical resistance	High electrical resistance
Electrolyte flammable, combustion hazard	Electrolyte nonflammable, safer
SEI layer forms and degrades, affects cycle life	No SEI layer formation, longer cycle life
Electrolyte reactions limit cathode materials	Electrolyte nonvolatile, high-voltage cathode materials
Poor thermal stability	Excellent thermal stability
Self discharge limits shelf life	Far less self discharge, much longer shelf life
Sensitive to overcharge	Abuse tolerant
Flexible separator hosts formation of lithium dendrites, limits cycle life	Ceramic separator inhibits dendrite growth, extended cycle life
More inactive materials, reduces energy density, reduces specific energy	Less inactive materials increases energy density, increases specific energy

Table 1 General comparison of liquid lithium-ion batteries with solid-state lithium-ion batteries. Challenges for the technology are shaded red, and advantages are shaded green.

internally, there is a dramatic improvement in operational safety. The inert nature of SSEs also allows for the use of higher-voltage cathode materials, which improves energy density.

Despite the opportunity to use high-voltage cathodes, there are still challenges with their use. Thus, most thin-film solid-state battery manufacturers still use more-traditional cathode materials, such as LiCoO_2 and LiMn_2O_4 . However, many do use metallic lithium as the anode. Likewise, solid-electrolyte interfacial layer formation and other secondary reactions during operation are reduced or even avoided in solid-state batteries, which results in very low self-discharge rates and allows for multi-year storage with minimal loss of power.

Additionally, prior work has shown that solid-state batteries can potentially cycle 10–100 times longer without fading than can liquid batteries. For example, Infinite Power Solutions (Littleton, Colo.) offers thin-film batteries that have been shown to cycle more than 10,000 times with little fading.

The stability of SSEs also allows

solid-state batteries to be charged and discharged at very high rates without unwanted side reactions, which increases the scope of application. Finally, SSEs are stable over a large temperature window, which allows for operation of solid-state batteries over a wider temperature range than typical lithium-ion batteries with liquid electrolytes. The relative advantages of solid-state batteries are summarized in Table 1.

Manufacturing and economic hurdles

Considering these distinct advantages, if higher-capacity cells could be made economically, solid-state batteries have great potential for personal mobility devices (recording devices, cell phones, tablets, laptops) and would appear to be an excellent choice for larger power applications, such as electric vehicles and some grid storage applications. Moreover, the electric vehicle battery market is forecast to quadruple during the next eight years.

However, for solid-state batteries to be feasible in such applications, several

factors need to be addressed. The primary concern is manufacturing cost, but there also are challenges with developing higher-capacity and higher-voltage cathodes, better anodes and integrating thicker films into a solid-state geometry.

At present, commercially available thin-film solid-state batteries are fabricated using vacuum-based deposition techniques, such as RF and dc magnetron sputtering. Traditionally, larger batteries rely on more conventional deposition processes, such as slurry coating and calendaring.

Therefore, because more complex equipment is currently required for solid-state battery manufacturing, the cost of fabrication of these cells is very high. For example, using contemporary technologies to scale up from milliamp-hour microbatteries to 1 amp-hour cells typical of a cell phone would result in a cost per battery of potentially thousands of dollars. Obviously, this is not practical. Therefore alternative technologies to vacuum-based deposition processes are needed.

In addition to manufacturing costs, evolving electrode materials may create a hurdle to solid-state batteries. There has been a significant amount of recent research into alternative cathode and anode materials. Basically, there are two classes of these materials: intercalation-type materials, where lithium atoms are stored interstitially without changing the crystal structure of the electrode (CoO_2 , for example); and substitutional materials, where lithium reacts with the electrode to create a compound with a crystal structure different from the delithiated material (silicon, for example).

The substitutional compounds offer tremendous improvements in the theoretical specific capacity, but may also experience significant volumetric changes during charging (lithiation) and discharging (delithiation).

In conventional batteries, electrodes synthesized with nanoscale features have been shown capable of accommodating large volumetric changes.¹⁶ In the case of solid-state batteries, the strain accommodation challenges associated with substitutional compounds

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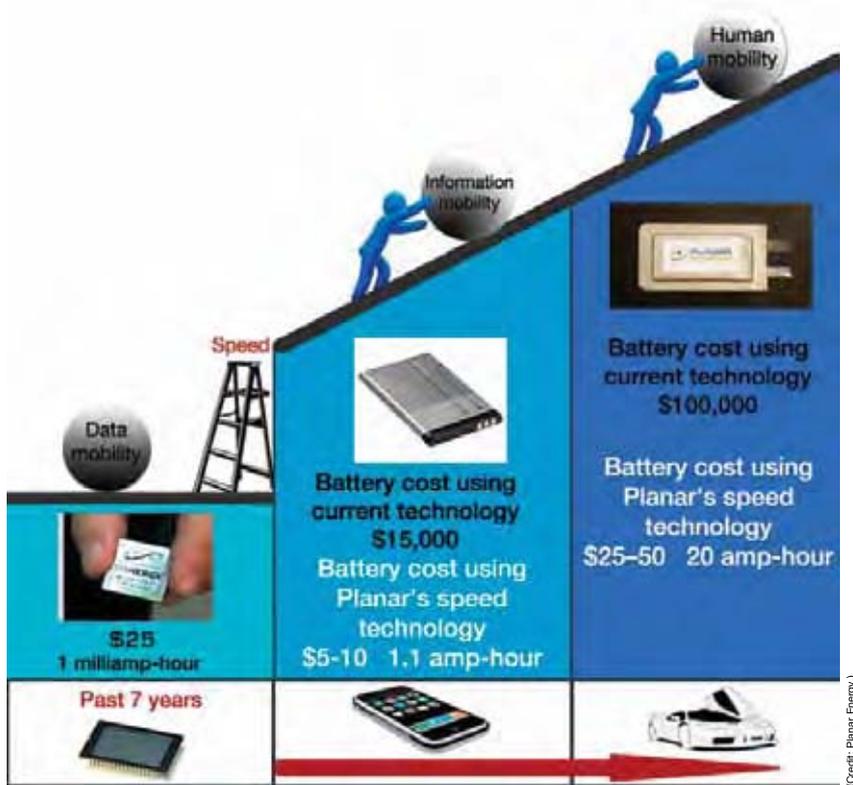


Figure 4 Solid-state technology is proven, but does not scale. Using current thin-film technology, the cost of a single 20-amp-hour battery would be \$100,000. A high range electric vehicle will require 800–1,000 20-amp-hour cells.

are potentially greater. In addition, with scale up comes the additional challenges of integrating conventional and thin-film technologies to maximize performance while minimizing cost [Figure 4].

Engineering toward applications

One of the greatest future opportunities for solid-state batteries is the electric vehicle market. The Advanced Research Projects Agency in Energy has identified a number of very specific targets that must be achieved to meet the future needs for electric vehicles. Two of ARPA-E's targets are that the cost of the batteries must be below \$250 per kilowatt-hour, and the specific energy of the completed battery must be greater than 200 watt-hour per kilogram.

There are several major challenges that must be solved before solid-state batteries can meet or exceed these goals. Planar Energy (Orlando, Fla.) won a grant from ARPA-E to develop solid-state cells for use in batteries for electric vehicle propulsion.

The work on this project identified three important requirements for the design of the cells:

- The cathode should be a composite material;
- The solid-state electrolyte should have conductivity of at least 10^{-4} siemens per centimeter; and
- The materials should be compatible with each other in structure and in chemical interactions.

These three requirements interact and require a delicate balance.

• There is no single solid-state cathode material that can store large amounts of lithium and which also has good ionic and electronic conductivity. Therefore, solid-state cells need cathodes with composite structures. The challenge of composite materials is the compatibility of their materials.

• In solid-state cells, the electrolyte functions as a separator. To be compatible with thick high-capacity cathodes, the electrolyte needs to be thicker than it is for thin-film batteries. Thus, the electrolyte needs to have a higher ionic

conductivity than LIPON. Based on experimental evidence, the electrolyte should have a minimum ionic conductivity of 10^{-4} siemens per centimeter, and it must be deposited in a way that minimizes the cell internal resistance. Many of the higher-ionic-conducting electrolytes are not good candidates for thin-film deposition. Planar Energy has developed a thio-LISICON-type solid-state electrolyte that has good ionic conductivity and high electrical resistance.

• The challenge of the cathode/electrolyte/anode interface is finding the right solid-state electrolyte that meets the three requirements; does not alloy with the cathode or anode materials; is structurally compatible with the cathode or the anode during charging and discharging; and has no built-in field at the cathode/electrolyte junction or the electrolyte/anode junction that could be detrimental to lithium-ion diffusion across the junction.

Many groups^{17,18} are currently working to solve these issues and create a high-capacity solid-state lithium-ion battery. One intriguing possible solution is to combine the technologies of solid-state and liquid lithium ion batteries. For instance, some of the limited ionic conductivity of thick-cathode and the structural incompatibility issues in large format solid-state cells with “cathode/SSE/Li” structure could be circumvented with the use of a so-called hybrid cell construction.

The hybrid cell is essentially a solid-state cell with a small amount of liquid electrolyte. In addition to working on a large format, all solid-state battery, Planar Energy is investigating a possible hybrid cell (see sidebar). Here, the cathode and the anode are independent of each other, as in traditional cells, but the cathode and the anode are each coated with solid-state electrolyte to form “cathode/SSE” and “SSE/Li” structures. These structures are brought together to form “cathode/SSE/drop of liquid/SSE/Li” hybrid cell structures.

Such a cell has a liquid electrolyte to ionically connect the anode to the cathode. The cell has no polymer separator. The SSE on the cathode and the anode form the inorganic separator of the cell.

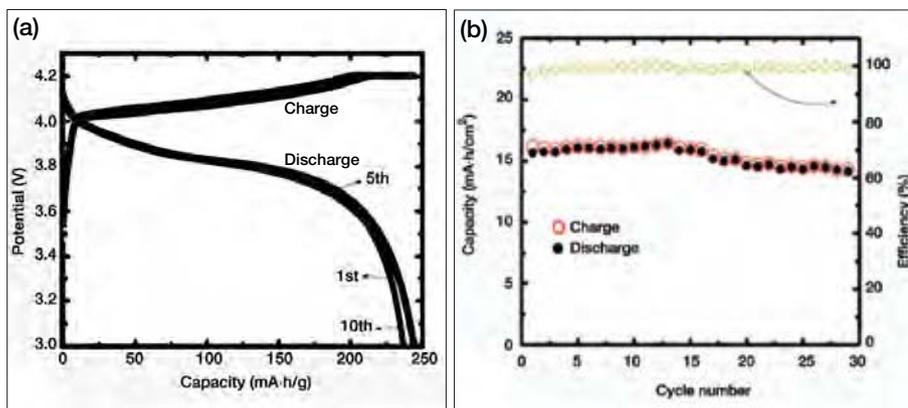


Figure 5 (a) Charge/discharge voltage profile of LiCoO₂-composite/SSE/.../SSE/L hybrid cell with the specific capacity of about 245 milliamp-hours per kilogram. (b) Charged-discharge capacity of the same cell showing an areal capacity of about 15 milliamp-hours per square centimeter. The cell was charged/discharged at 2 milliamps per square centimeter.

The SSE coatings on the electrodes block SEI layer formation, giving the cell a much longer cycle life. Because all materials in the cell are inorganic, except for the liquid electrolyte, there are no observed side reactions, and self-discharge is negligible. The small amount of liquid makes the cell very safe.

Figure 5 shows the performance of a LiCoO₂ composite hybrid cell (“LiCoO₂-composite/SSE/drop of liquid/SSE/Li”); fabricated with Planar Energy’s SPEED deposition system. The system uses water-based, electroless techniques to grow thin or thick films at high rates on any hydrophilic substrate.^{19–21} The cell has an areal capacity of 15 milliamp-hours per square centimeter, with a corresponding specific capacity of 245 milliamp-hours per gram with respect to LiCoO₂ content of the cathode, which is imbedded in a nickel foam. This capacity is higher than LiCoO₂ normally exhibits, and it is possible the additional capacity comes from cation additives intentionally introduced into the LiCoO₂. Further studies are in progress to understand and optimize this.

By combining the lower reactivity of a solid-state electrolyte with the higher interfacial connectivity of the liquid electrolyte, we can start to realize larger solid-state batteries. This approach is just one alternative to making higher-capacity solid-state batteries.

These results suggest that to bridge the gap from microbatteries to larger batteries, in the short term, it may take

a hybrid approach. This approach takes advantage of the best attributes of the liquid and solid-state battery systems to achieve its goal.

Summary

Interest in solid-state batteries is increasing rapidly because they offer numerous advantages over traditional liquid-based batteries. Yet, to expand the application of solid-state batteries from the realm of microbatteries, several issues and hurdles need to be addressed. If these issues can be successfully addressed, then the future for solid-state batteries is enormous. ■

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