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LITHIUM-ION BATTERIES

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MEET THE AUTHORS

MICHELLE BRYNER is a senior editor at *Chemical Engineering Progress* (Email: michb@aiche.org), where she covers topics ranging from traditional chemical engineering to metamaterials and nanotechnology, to supercomputer advancements, to biotechnology. She has written for *Popular Science* and *Psychology Today,* as well as the online publications TechNewsDaily.com, InnovationNewsDaily.com, and MensHealth.com. Before becoming a writer, she worked as a chemical engineer at W.L. Gore, where she developed new processes and products (including some of the PacLite gear). She received a BChE from the Univ. of Delaware and an MS in science journalism from New York Univ., and is a member of AIChE.

GERRY M. CLARKE, CEng is a scientist and consultant on industrial minerals (Phone: +44 (0)20-8224-5553; Email: gmclarke1@ntlworld.com). Previously, he was an executive director of Metal Bulletin plc, a London-based company that provides business information services to the international metals, minerals, and financial communities. Since retiring from corporate life in 2005, he has focused on research for publication, consulting, and speaking engagements on fluorspar, magnesia, lithium, rare earths, and specialty metals. He created and self-published lithium availability wall maps that were presented to the Advanced Automotive Battery Conference and Exhibition in Long Beach, CA (in 2009), and in Mainz, Germany (2010). He holds a BSc in mining engineering and geology and an MSc in applied mineralogy from Univ. of Wales, Cardiff, and was a lecturer in earth resources at Plymouth Univ. in the U.K. He is a member of the Institution of Materials, Metals, and Mining (IOM3) and is a Chartered Engineer.

ANDREW N. JANSEN, PhD, is a principal chemical engineer in the Chemical Sciences and Engineering Div. of Argonne National Laboratory (9700 South Cass Ave., Argonne, IL 60439; Phone: (630) 252-4956; Email: jansen@anl.gov) with more than 20 years of experience in research and development of advanced battery systems. Much of his research has centered on the use of lithium-based batteries, such as lithium-alloy/iron disulfide, lithium polymer, and lithium-ion batteries for transportation applications. He has recently expanded his interests to include grid energy storage. He is the team leader of the Cell Analysis, Modeling, and Prototyping (CAMP) Facility at Argonne, which is focused on the advancement of novel high-energy cell systems. He holds three chemical engineering degrees: a PhD from the Univ. of Florida, an MS from the Univ. of Virginia, and a BS from the Univ. of Wisconsin-Madison.

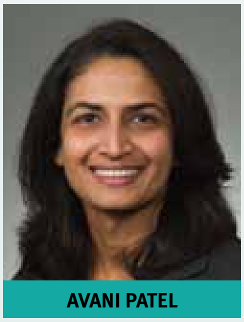
AVANI PATEL is the Associate R&D Director for Dow Energy Materials (Email: ampatel@dow.com), where she leads the organization's research and development of next-generation battery materials and components for lithium-ion battery applications. She previously held a variety of technical and management positions at Dow, including Senior Technical Manager for Reaction Engineering, and Technology Leader for Biosciences, as well as assignments in Dow Building Solutions, and in Engineering Sciences and Market Development. She has a BS in chemical engineering from Michigan State Univ., a BS in biochemistry from St. Xavier's College of Gujarat Univ., India, and a degree in medical technology from Gujarat Cancer Research Institute, India. She is also a certified Six Sigma black belt and is a member of AIChE.

ROBERT SPOTNITZ, PhD, leads Battery Design LLC, a company that develops software for battery design and simulation (Phone: (925) 399-1796; Email: rspotnitz@batdesign.com; website: www.batdesign.com), and is a well-known speaker on battery engineering. In 2009, he partnered with CD-adapco to support Battery Design Studio, a virtual environment for battery design and simulation (www.cd-adapco.com/products/battery-design-studio). He has also participated in the startup of two battery developers: American Lithium Energy Corp. and Enovix Corp. Before starting Battery Design, he was a director at Poly-Stor, where he led efforts to develop li-ion batteries for hybrid electric vehicles. Previously, he worked for Hoechst, where he started a battery applications laboratory, and at W. R. Grace, where he made several inventions, including the multilayer battery separator that is widely used today. He received a BS in chemical engineering from Arizona State Univ., an MS in computer science from Johns Hopkins Univ., and a PhD in chemical engineering from the Univ. of Wisconsin-Madison. He is a member of the Electrochemical Society and the International Society of Electrochemistry. He has been awarded 23 patents and has 38 publications, including four book chapters.


MICHELLE BRYNER


GERRY M. CLARKE


ANDREW N. JANSEN


AVANI PATEL


ROBERT SPOTNITZ

LITHIUM-ION BATTERIES

Michelle Bryner
Senior Editor

Batteries are being asked to meet daunting performance requirements that could soon be pushing up against the limits of existing battery technologies. Portable electronics, electric vehicles, and grid-scale storage require high energy density and power, low cost, and safety.

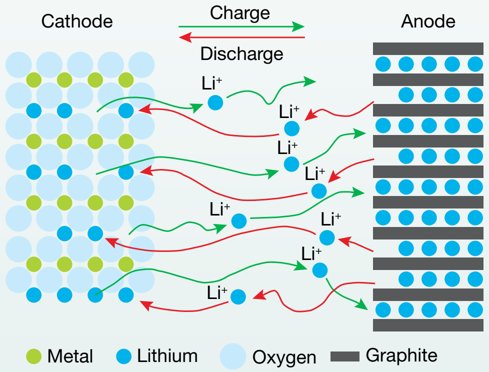
The ever-increasing function coupled with the shrinking size of portable electronics, the integration of renewable energy into the power grid, and the trend toward all-electric vehicles are weighing heavily on battery technology.

Manufacturers of batteries for mobile phones, tablets, and laptops are continually being called upon to pack more and more power into smaller and smaller form. Moore's Law has enabled the computing power that was once housed in a building to fit into a pocket-size device — putting pressure on the batteries that power these devices to follow suit. The problem is that the charge carriers in a battery (lithium ions) are much larger than electrons, which are the charge carriers in electronics. Thus, battery size is restricted by the relatively bulky ion.

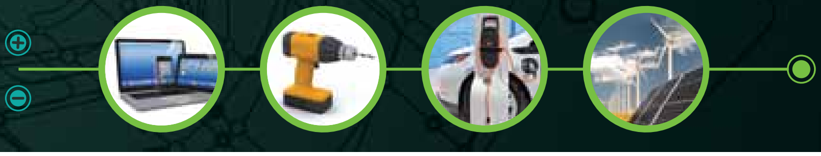
Electric vehicles fall into three categories — hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and battery electric vehicles (BEVs) — each requiring slightly different battery performance. The automotive industry requires batteries that pack enough energy to allow for long-range driving coupled with a high power density for acceleration, and these batteries must be lightweight, low cost, ultrasafe, and able to cycle thousands of times.

The lithium-ion battery is not the only energy-storage device being considered for backing up the power grid. Others include supercapacitors, pumped hydro, flywheels, and compressed-air energy storage (CAES), as well as alternative battery technologies such as flow batteries, sodium sulfur (NaS) batteries, and advanced lead-acid batteries. Funded by the U.S. Dept. of Energy (DOE), the Pacific Northwest Smart Grid Demonstration Project is evaluating Li-ion batteries and other power-grid storage technologies. As part of that effort, a 5-MW lithium-ion battery storage unit was unveiled in June of this year at Portland General Electric's Salem Smart Power Center in South Salem, OR — the largest grid-scale battery unit being tested.

Batteries store energy in the form of chemicals and convert this chemical energy into electrical energy on demand. The basic unit of a battery is the electrochemical cell, which consists of an anode and a cathode separated by an electrolyte. These cells are typically combined in series or parallel to form modules, which are then connected (also



▲ **Figure 1.** The electrodes of Li-ion rechargeable batteries typically consist of layered materials to allow for the insertion of lithium ions. During charge and discharge, lithium ions move back and forth between the anode and cathode. But instead of breaking and making bonds, these ions simply move into and out of the structure of the electrodes.



in series or parallel) to form packs. Packs also contain the necessary electronics (*e.g.*, sensors, voltage converter, and regulator circuit) to facilitate safe and reliable operation.

The Li-ion battery

The components of the cell determine whether a battery is rechargeable (secondary) or nonrechargeable (primary), as well as how much energy it can store (energy density), how fast it can charge and discharge (power density), its cycle life, safety, and cost. Among rechargeable batteries, the lithium-ion battery has become the battery of choice.

Rechargeable batteries came on the scene in 1859 with the invention of the lead-acid battery, followed by the nickel-cadmium battery in 1899. Both battery chemistries are still in use today. Two new rechargeable battery chemistries, which offer much higher energy density than their predecessors, were developed over the past two decades: the nickel metal hydride battery (1990), and the Li-ion battery (1991).

The lithium-ion battery offers many advantages over other rechargeable battery technologies. Li-ion batteries boast high energy densities (typically twice that of NiCd batteries) and high cell voltages (3.6 V). They require little maintenance, do not experience memory effects, and exhibit relatively low self-discharge.

Lithium-ion batteries come in a variety of chemistries, but their principle of operation is the same (Figure 1). The anode undergoes oxidation, releasing electrons, while the cathode is reduced by those electrons. Lithium ions move between the two electrodes through the electrolyte, and the electrons travel to an external electric circuit to charge or power a device. (The electrolyte is electronically insulating and therefore blocks electrons from passing through it.)

Battery chemistry and design are dictated by the performance requirements of the application of interest. While consumers would like every battery for every application to have the best of all attributes — energy density, power density, safety, lifetime, and cost — tradeoffs exist that make this impossible. Instead, some batteries are designed for high power, some for high energy capacity, and so on.

Energy density, which describes the amount of electricity the battery can deliver, is largely governed by the choice of cathode material. On the other hand, power density, which quantifies the rate at which a battery delivers electric current, depends on the materials used for the electrolyte and both electrodes. Because there are many ways for a battery to fail, most of the components within the battery will influence the lifetime. Safety — a key concern for designers of lithium-ion batteries — relates to the thermal stability of the electrodes: At high temperatures, the electrode materials degrade into compounds that can react with a flammable organic electrolyte.

BATTERY MILESTONES

The development of today's batteries has been in the works since the 1700s. Many milestones along this road are highlighted in this timeline.

1799	Alessandro Volta demonstrates the first electrochemical cell in the form of a stack of alternating zinc and copper discs with brine-saturated cloth placed between the disks.
1836	British chemist John Frederic Daniell invents the first practical battery device, consisting of two half-cells separated by a salt bridge. He fills an earthenware container with sulfuric acid and a zinc electrode, and places it in a copper pot filled with a copper sulfate solution.
1859	Gaston Planté creates a lead-acid battery that consists of two sheets of lead separated by rubber strips, rolled into a spiral, and immersed in a sulfuric acid solution.
1866	Georges Leclanché invents the zinc-carbon "wet" cell, which consists of a zinc anode, a cathode of carbon and manganese dioxide, and an ammonium chloride solution as the electrolyte.
1899	Waldmar Jungner invents the nickel-cadmium battery. The NiCd battery used today relies on a modified version of this chemistry.
1913	Gilbert Lewis demonstrates for the first time the potential of lithium as a battery electrode.
1947	Georg Neumann proposes changes to Jungner's NiCd battery that allow for the construction of a sealed battery. To prevent the pressure within the battery from increasing due to the buildup of oxygen (generated at the cathode) and hydrogen (generated at the anode), he creates a larger anode, which mitigates the amount of hydrogen gas generated and increases the efficiency of oxygen absorption.
1960	NASA and the U.S. Dept. of Energy develop the first primary lithium-metal battery.
1980	John Goodenough invents the lithium cobalt oxide cathode, which was later used in the first Li-ion rechargeable battery commercialized by Sony in 1991.
1980s	Akira Yoshino, working at Asahi Kasei Corp., conceives of the first Li-ion rechargeable battery with a solid electrolyte in the early 1980s and makes the first working prototype in 1986. The battery uses lithium cobalt oxide for the cathode; a carbonaceous material as the anode; a nonaqueous electrolyte consisting of lithium hexafluorophosphate ($LiPF_6$) or lithium tetrafluoroborate ($LiBF_4$) dissolved in a mixture of carbonate compounds; and an aluminum foil current collector.
1990	The nickel metal hydride rechargeable battery is commercialized.
1991	Sony Corp. commercializes the first Li-ion rechargeable battery.

Article continues on next page

Engineering a better Li-ion battery

If batteries were able to meet all of the demands of all of their existing and future applications, they would not be the topic of a *CEP* energy supplement. So, while lithium-ion batteries represent a step up from older chemistries and they themselves have made significant improvements over the past two decades, there is still much more to be done.

Energy density, power, and lifetime. Efforts are underway to develop new materials and designs to boost the performance of Li-ion batteries. One area that continues to receive significant attention is the cathode material, as it largely determines the energy density of the battery. Several alternative cathode materials are being explored.

The anode material must be compatible with any new cathode material and be able to accept the increased number of lithium ions that a new cathode material would provide. Thus, researchers are also looking at new anode materials. In theory, silicon anodes provide a tenfold increase in capacity over graphite in Li-ion batteries. The problem, however, has been the large volume changes that silicon undergoes during charging and discharging, which causes cracks to form in the anode.

Safety. Safety features are incorporated within the lithium-ion battery pack to minimize risks associated with this type of battery. However, the need for extreme safety in electric vehicles has energized research efforts to find a more stable electrolyte. (At high operating temperatures, degradation products in the battery can react with the flammable electrolyte, which typically consists of lithium salt dissolved in an organic solvent.) The safety issues associated with Li-ion batteries are evidenced by several incidents aboard Boeing 787 planes involving thermal runaway of the lithium-ion batteries.

Cost. Lithium-ion batteries are more expensive than other rechargeable batteries — a disadvantage that particularly impacts their use in electric vehicles and grid-scale storage. Several of the materials used to make the electrodes (*e.g.*, lithium, cobalt, and nickel) are expensive and require costly methods to extract and process them into usable forms. One potential strategy for reducing the cost of Li-ion batteries would be to develop new extraction and processing methods that are less costly.

Focusing on Li-ion batteries

Batteries present many opportunities for chemical engineers to bring their skills to bear. From the mining and processing of raw materials (*e.g.*, lithium, cobalt, and carbon), to developing better electrode materials through nanotechnology, to component assembly, chemical engineers have the unique skills and training necessary to design next-generation batteries to meet the demands of future applications. This special section provides an overview of lithium-ion batteries, introducing the basic concepts involved in batteries and identifying areas where further development is necessary.

In the first article, Robert Spotnitz of Battery Design LLC sets the stage with some basic information about batteries. He discusses the main components of batteries, emphasizing the role of each and introducing some of the issues that must be considered in the design of these components. Spotnitz works through the thermodynamics and kinetics that characterize electrochemical cells, and he uses fundamental equations to explain limits on performance and to compare the performance of existing battery systems to what could be achieved with good engineering.

In the second article, minerals consultant Gerry Clarke covers the major raw materials that go into Li-ion batteries. He identifies the major resources found around the world, and discusses the challenges related to the mining and production of these raw materials. The article focuses mainly on lithium — the essential ingredient of Li-ion batteries — and addresses recent speculation that the Earth's lithium resources will not be sufficient to meet the rising demand for this metal. The processes for extracting lithium and converting it into lithium carbonate, the primary lithium chemical used to produce lithium-based battery components, are also discussed.

Lithium-ion batteries can be made in a wide variety of cell designs using different combinations of materials. This is the topic of the third article, in which Avani Patel, R&D Director for Dow Energy Materials, discusses the materials used to create Li-ion battery electrodes, ion conductors, and separators. Patel points out that many material combinations are available to cell designers, and that optimizing the pairing of key materials can significantly impact cell performance for a target application.

In the final article, Andrew Jansen of Argonne National Laboratory rounds out the supplement by exploring battery applications, including transportation, portable electronics, and massive electricity storage. Jansen ties together some of the topics introduced in the preceding articles, such as the selection of materials for the electrodes and the performance metrics.

In discussing battery applications, Jansen concludes that the lithium-ion battery will not be able to meet the demands of future-generation applications. While advances continue to provide incremental improvements to the performance and cost of lithium-ion batteries, it is time to look beyond this technology to what is next. Jansen notes several areas of interest, including multivalent intercalated ions that carry more charge than lithium; chemical reactions of the working ion to store more energy; and nonaqueous redox flow systems. CEP

LITHIUM-ION BATTERIES
The Basics

Robert Spotnitz
Battery Design LLC

Batteries come in a variety of chemistries and designs. Using fundamental principles, the theoretical performance of these electrochemical cells can be determined, enabling you to engineer the optimal device.

Providing power in applications ranging from digital cameras and cellphones to electric vehicles and renewable-energy storage, batteries convert chemical energy into electrical energy to produce a direct current. While batteries come in a range of designs with a variety of chemistries, their basic anatomy and operation are the same. Each consists of a positive electrode, an ion conductor (electrolyte), and a negative electrode, which undergo chemical reactions to produce electricity.

This article provides an introduction to the chemistry and design of batteries. It discusses the major battery components, explaining their roles and how each contributes to the battery's performance and safety. Although the article touches on several battery types, it focuses mainly on lithium-ion batteries. References 1–3 provide more information beyond the scope of this article.

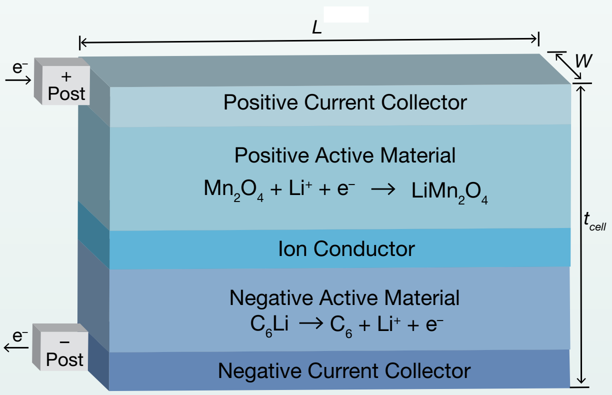
Under the battery's hood

Figure 1 illustrates the structure of a typical lithium-ion battery. Each electrode consists of an active material in the form of a paste or coating on a metal current collector. The essential feature of the active material is that it undergoes an electrochemical, or charge-transfer, reaction at its interface with the ion conductor:

$$Li^+ + e^- \leftrightarrow Li^0 \qquad (1)$$

The positive active material (*i.e.*, cathode) is reduced by electrons from the external circuit, while the negative active material (*i.e.*, anode) is oxidized, releasing electrons that travel through the external circuit. The potential difference between the anode and the cathode is the voltage. The ion conductor provides a medium for the ions to travel between the two electrodes, but because it is electronically insulating electrons cannot pass through it. The current collectors connected to the electrodes provide paths for the electrons to travel to the external electric circuits.

Batteries can be classified as primary or secondary, and are sometimes classified as aqueous or nonaqueous. A primary battery is discharged once and discarded, while a secondary battery can be recharged. Aqueous batteries use water as the solvent for the ion-conducting phase (*e.g.*, sulfuric acid), while nonaqueous batteries use organic liquids with dissolved salts (*e.g.*, lithium hexafluorophosphate in



▲ **Figure 1.** A typical Li-ion battery consists of positive and negative electrodes, current collectors, and an ion conductor.

a mixture of ethylene carbonate and dimethyl carbonate), ion-conducting polymers (*e.g.*, polyethylene oxide), or inorganic ion conductors (*e.g.*, lithium phosphorus oxynitride or lithium superionic conductor). The distinction between aqueous and nonaqueous batteries has recently become blurred with the introduction of aqueous lithium batteries, which use an inorganic solid electrolyte to shield the lithium against an aqueous electrolyte that contains the positive electrode.

Battery chemistry and energy density

The energy density of a battery is the product of the cell's voltage and specific capacity, which are determined by the chemistry of the electrodes. The electrochemical reaction at each electrode establishes a voltage in the metal current collector that can be measured with respect to a second electrode. By convention, potentials of electrochemical reactions (E^o) are reported with respect to a standard hydrogen electrode (Table 1). The cell voltage is the difference in the potential of alkali ions on the two electrodes. For example, a cell that pairs Ag_2O reduction ($E^o = 0.342$ V) with Zn metal oxidation ($E^o = -1.285$ V) has a voltage of 1.627 V.

Of special interest to modern batteries are so-called "insertion" reactions, where one species, such as a lithium cation, inserts itself into a structure, like graphite. Graphite has a layered structure, and lithium ions can diffuse into the space formed between the graphite layers. Insertion reactions are highly reversible, allowing thousands of charge/discharge cycles. There is an ongoing effort to develop new insertion materials that provide higher energy density.

Lithium-ion batteries use lithium insertion reactions at both the positive and negative electrodes. In contrast, conventional batteries typically involve the formation and destruction of covalent bonds and massive structural changes. For example, the discharge of a silver-zinc battery involves the reduction of silver oxide (Ag_2O) to silver metal at the positive electrode and zinc metal oxidation to zinc oxide (ZnO) at the negative electrode; both of these reactions involve breaking and forming atomic bonds and massive changes in electrode volume.

Table 1. The voltages of electrochemical materials used in battery electrodes are referenced to a hydrogen electrode.

Reaction	E^O, Volts
$F_2 + 2e = 2F^-$	2.87
$Cl_2 + 2e = 2Cl^-$	1.36
$PbO_2 + SO_4^{2-} + 4H^+ + 2e = PbSO_4 + 2H_20$	1.685
$O_2 + 4H^+ + 4e = 2H_2O$	1.229
$Ag_2O + H_20 + 2e = 2Ag + 2OH^-$	0.342
$2H^+ + 2e = H_2$	0
$Pb^{2+} + 2e = Pb$	–0.13
$Cd^{2+} + 2e = Cd$	–0.43
$Zn^{2+} + 2e = Zn$	–0.76
$Zn(OH)_2 + 2e = Zn + 2OH^-$	–1.285
$Li^+ + e = Li$	–3.05

A key area of development for batteries is maximizing energy density.

The voltage corresponding to a given charge-transfer reaction can be related to the Gibbs free energy of reaction (ΔG), or useful work:

$$\Delta G = -nFE^o \tag{2}$$

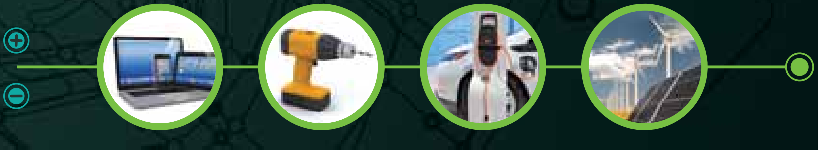
where E^o is the cell voltage (V), n is the number of electrons involved in the reaction, and F is Faraday's constant (96,487 coulomb/mole of electrons [C/mol]). Unlike thermal processes that obey Carnot cycle limitations, the free energy of a charge-transfer reaction can be completely converted into useful work.

A major challenge in battery development is to maximize energy density, both gravimetric and volumetric, as many applications constrain the size and/or weight of the battery. For consumer applications, such as cellular phones, volumetric energy density is typically the major concern. The best Li-ion cells for consumer electronics today have volumetric energy densities of about 550 Wh/L. For military applications, which typically involve a soldier carrying a battery pack, gravimetric energy density is typically the most important metric. The best lithium-ion cells for these applications have gravimetric energy densities of around 250 Wh/kg. For automotive applications, volume and weight are both important. The best lithium-ion cells for hybrid electric vehicles (HEVs) have energy densities of about 75 Wh/kg and 100 Wh/L, while the best lithium-ion cells for battery electric vehicles (BEVs) have energy densities of about 160 Wh/kg and 320 Wh/L.

Batteries with high voltages can be constructed by selecting appropriate positive and negative electrode reactions. Table 1 shows that the highest possible voltage is obtained by coupling lithium oxidation with fluorine reduction. Because water is unstable at high voltages, the ion conductor, which connects the two electrodes, must be nonaqueous to achieve high cell voltages (>2.1 V).

The theoretical gravimetric energy density (ED_{grav}) is given by:

$$ED_{grav} = \frac{nF\left(E^o_{pos} - E^o_{neg}\right)}{EW_{reactants}} \tag{3}$$



where $EW_{reactants}$ is the equivalent weight (g/g-mol) of the reactants. The theoretical gravimetric energy density of the lithium oxidation and fluorine reduction pair is calculated from Eq. 3 as:

$$ED_{grav} = \frac{(96{,}487\text{ C/mol})(2.87\text{ V} - (-3.05\text{ V}))}{(3{,}600\text{ s/h})(6.941\text{ g/mol} + 19.0\text{ g/mol})} \qquad (4)$$

$$= (6.106\text{ Wh/g})\ (1{,}000\text{ g/kg}) \ = \ 6{,}106\text{ Wh/kg}$$

This calculation uses the unit conversion that 1 W is equal to 1 volt-coulomb/s (V-C/s). This theoretical value does not account for losses incurred in the ionic conductor, current collectors, or packaging, so this number typically is divided by a factor of two to estimate a practical energy density of 3,053 Wh/kg. While the lithium-fluorine electrode pair example provides an upper limit on achievable voltage, it is not a practical battery chemistry because of the difficulties involved in handling fluorine. In comparison, the highest energy density achieved in a rechargeable Li-ion battery today is about 250 Wh/kg (vs. the theoretical limit of 574 Wh/kg). Nature allows much higher energy density batteries than are presently available, which means that a real opportunity exists to develop such batteries through engineering.

The lithium-fluoride battery provides a theoretical maximum cell voltage of 5.92 V, whereas the voltage of typical Li-ion batteries is 2.5–4.2. The most commonly used negative electrode for Li-ion batteries is graphite, which operates close to the voltage potential of lithium metal — the low-voltage limit of electrochemical reactions. Thus, there is little opportunity to increase cell voltage by lowering the voltage of the negative electrode. (Thermodynamically, one would expect graphite to react with nonaqueous solvents at low voltages, and thus not be a useful electrode material. However, some solvents, notably ethylene carbonate, react with graphite to form a solid electrolyte film on the surface of the negative electrode. This film inhibits further reaction while enabling lithium-ion transport.)

Inspired by the success of using the solid electrolyte film to address issues with the graphite negative electrode, several researchers are exploring the use of thin films to protect other active materials. One goal of this work is to develop thin films to stabilize positive electrodes and enable battery operation at 5 V, which would substantially increase the energy density of Li-ion batteries.

Cell design, kinetics, and power density

The energy density (Wh/kg or Wh/L) indicates the amount of energy a battery of a specific size (weight or volume) might provide, while the power density (W/kg or W/L) indicates the rate at which that energy can be delivered. The cell chemistry sets an upper limit on the energy density of a battery, while the cell design and kinetics determine the power density.

The lithium-fluorine electrode pair provides an upper limit on the voltage that can be achieved in a Li-ion battery.

The kinetics of charge-transfer reactions are similar to chemical reaction kinetics in that they both follow the law of mass action (a mathematical model for the behavior of solutions in dynamic equilibrium) and the Eyring equation, which relates the reaction rate to temperature. They differ in that the activation energy of charge-transfer reactions depends on the potential difference across the electrode/electrolyte interface. Electrochemical reactions, like chemical reactions, often involve catalytic effects.

A good indicator of the reversibility of battery kinetics is the exchange current density (i_0, A/m^2), which is the current flowing at equilibrium when the oxidation and reduction reactions are proceeding at equal rates. Exchange current densities can vary from 10^4 A/m^2 to10^{-8} A/m^2; values for rechargeable battery materials are typically in the range of 10^4–10^{-2} A/m^2. The larger the exchange current density, the more reversible the reaction will be, and thus the more suitable for rechargeable batteries. Reactions with low exchange current densities can be used in single-use (primary) batteries.

The deviation of the voltage from its equilibrium value is called polarization, or overpotential (η):

$$\eta = E - E^o \qquad (5)$$

where E is the operating voltage of an electrode (V) and E^o is the equilibrium voltage (V). The overpotential is related to the net rate of a charge-transfer reaction by the Butler-Volmer equation:

$$i = i_0\left(\exp\left(\frac{\alpha_a nF}{RT}\right) - \exp\left(\frac{-\alpha_c nF}{RT}\eta\right)\right) \qquad (6)$$

where i is the net current per unit area of electrode (A/m^2), α_a is the dimensionless anodic transfer coefficient, α_c is the dimensionless cathodic transfer coefficient, R is the ideal gas constant (0.00831 kJ/mol-K), and T is the temperature (K). The electrode transfer coefficients (α_a and α_c) quantify the fraction of electrical energy across the interface between the electrode and ion conductor that drives the charge-transfer reactions. The Butler-Volmer equation assumes that the current produced in the electrochemical cell depends exponentially on the overpotential. However, the rate at which a battery can charge/discharge is more often limited by mass- and charge-transport processes rather than by charge-transfer kinetics.

Ohm's law can be used as a first approximation of the voltage loss associated with charge transport. Consider the battery shown in Figure 1. The resistance of the positive collector ($R_{pos,\ coll}$) can be estimated by:

$$R_{pos,coll} = \frac{\rho_{pos}\left(L/2\right)}{t_{pos,\,coll}\,W} \tag{7}$$

where L is the length that the current must travel (m), ρ_{pos} is the resistivity of the positive collector (ohm-m), t is the thickness of the collector (m), and W is the width of the collector (m). Fortunately, highly conductive metals such as aluminum and copper with electronic conductivities of about 10^7 siemens/m (S/m) can often be used for collectors and posts (metal studs that protrude out of the battery stack). Thus, collectors with low resistances can be made using thin metal foils (about 10–30 µm thick).

In Li-ion batteries, the ionic conductor typically contains a support material called a battery separator. The porosity (ε) and tortuosity (τ) of this material must be accounted for by:

$$R_{ioncond} = \left(\frac{\rho_{ioncond}\, t_{ioncond}}{LW}\right)\left(\frac{\tau}{\varepsilon}\right) \tag{8}$$

where $t_{ioncond}$ (m) is the thickness of the porous separator (the ion conductor fills the pores of the separator), L is the length of the separator (m), and W is the width of the separator (m). The τ/ε ratio varies within the range of 2–12 for most battery separators. The resistivity of the ion conductor ($\rho_{ioncond}$) can be significant, so the use of thin separators (about 12–30 µm thick) is essential. Lithium-ion batteries use nonaqueous electrolytes, such as $LiPF_6$ in a mixture of ethylene carbonate and ethyl methyl carbonate, that are about 100 times more resistive than the aqueous sulfuric acid electrolytes used in lead-acid batteries.

To understand what limits the power of batteries, in addition to the voltage loss associated with charge transport, the effect of mass transport on the charge (or discharge) rate must be considered. A simple model for mass-transfer-limited current density (i_d, A/m^2) is:

$$i_d = \frac{FD_{eff}\,c}{\delta} \tag{9}$$

where D_{eff} is the effective diffusion coefficient (m^2/s), c is the concentration of either the lithium salt in the electrolyte or the solid-phase lithium sites (mol/m^3), and δ is the diffusion length (m). In a Li-ion battery, diffusion limitations can occur due to salt transport in the ionic phase that spans the entire cell and to lithium transport within the active materials of the negative and positive electrodes.

Electrolyte. Let's first consider transport in the ion-conducting phase (electrolyte). Nonaqueous electrolytes used in Li-ion cells have low salt diffusivities (about 10^{-6} cm^2/s) and lithium-ion transport numbers (about 0.4). The lithium-ion transport number indicates the fraction of net charge transported in the electrolyte by the lithium ion; if the value is less than one, a salt concentration gradient will form. A low salt diffusivity exacerbates the concentration gradient. Practically, the only way to operate batteries at useful rates with nonaqueous electrolytes is to use thin electrodes (<100 µm) and separators (<30 µm). However, the use of thin electrodes significantly reduces energy density.

For example, consider a battery with positive and negative current collectors that are 10 µm thick, a 20-µm separator, and 80-µm-thick positive and negative coatings. The volume fraction of active material (coatings) is 80% (the sum of the active coating thicknesses divided by the total thickness of all the layers). If the thickness of the coatings could be increased to 200 µm, then the fraction of active material would increase to 90%.

In addition to limiting energy density, the use of nonaqueous electrolytes introduces significant safety concerns. A typical electrolyte consisting of $LiPF_6$ in ethylene carbonate and ethyl methyl carbonate has a flash point of only 25.5°C and will give off significant heat if burned. Any incident that breaks the battery's hermetic seal allowing air to contact the electrolyte could result in a fire. Likewise, an internal short circuit might generate enough heat to initiate a reaction between the electrolyte and the active materials in the battery. Improving the safety performance of electrolytes is a major challenge for Li-ion battery designers.

Electrodes. Next, the mass-transfer limitations due to solid-phase transport can be considered. Solid-phase diffusion coefficients are typically about 10^{-13} m^2/s. As previously discussed, the electrode coatings must be substantially thicker than the separator and current collectors in order to realize significant volumetric energy densities. For a monolithic nonporous electrode such as that shown in Figure 1, Eq. 9 can be used to estimate the highest possible discharge rate. Consider a $LiMn_2O_4$ layer that is 60 µm thick. Equation 9 (with δ = 60/2 µm) indicates that solid-phase diffusion would limit the rate capability severely:

$$\frac{\text{A-h}}{\text{m}^2} = \frac{(96{,}487\ \text{C/mol})(24{,}731\ \text{mol/m}^3)(6\times10^{-5}\ \text{m})}{(3{,}600\ \text{s/h})} \tag{10}$$

$$= 40\ \text{A-h/m}^2$$

$$\frac{\text{A}}{\text{m}^2} = \frac{(96{,}487\ \text{C/mol})(24{,}731\ \text{mol/m}^3)\,(10^{-13}\ \text{m}^2\text{/s})}{\left(\dfrac{6\times10^{-5}}{2}\right)\text{m}} \tag{11}$$

$$= 8\ \text{A/m}^2$$

The theoretical lithium concentration of 24,731 mol/m^3 for $LiMn_2O_4$ is used. The "C rate" is defined as the ratio of current to capacity. For this example, the maximum C rate is 0.2 h^{-1}, which is very low. For consumer electronics applica-

tions, a maximum C rate of 2 h^{-1} is typically required.

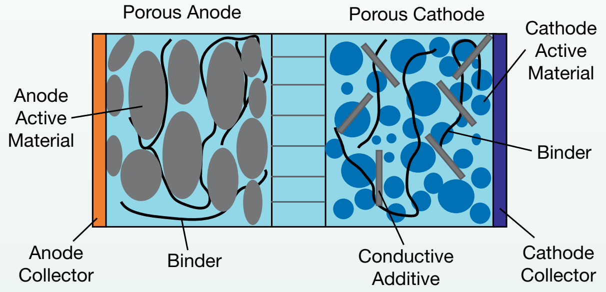
A practical way to achieve reasonable power in Li-ion batteries is through the use of porous electrodes *(4)*. A porous layer of $LiMn_2O_4$ comprised of fine particulates of active material (1–20 µm dia.) can create a relatively thick layer (*e.g.*, about 80 µm, before liquid-phase transport becomes limiting). The fine particles enable fast solid-phase transport by reducing the diffusion length, while the porosity enables access to the solid via liquid-phase transport. Thicker and less-porous layers maximize energy density, while thinner and more-porous layers maximize power density. Typical coatings of the particulate material are 40–90 µm thick and 20–40% porous. Figure 2 shows a practical Li-ion cell design using porous electrodes.

Other components

Batteries contain several other components in addition to the electrode materials and the ion conductor, such as separators, current collectors, packaging materials, and additives.

Separators. Separators prevent electronic contact between electrodes while allowing ionic transport. However, separators used in Li-ion batteries are not simply porous dielectrics filled with an electrolyte. They are often multilayer, microporous structures that, in addition to providing a medium for ionic transport, also enhance safety by preventing ion transport at elevated temperatures (>130°C) and providing mechanical stability at high temperatures (>200°C).

Current collectors. Copper foils are typically used as negative current collectors and aluminum foils as positive collectors. The surfaces are often specially treated to promote adhesion to the active material coating. For example, aluminum current collectors are sometimes coated with a thin carbon layer (<3 µm) to reduce contact resistance with the active material paste, or with proprietary coatings filled with positive-temperature-coefficient materials whose resistance increases with temperature to provide a safety benefit.



▲ **Figure 2.** The Li-ion battery shown in Figure 1 does not represent a practical battery structure, as the electrodes are monolithic layers. A more practical Li-ion cell consists of porous electrodes filled with electrolyte (light blue), particles of active material (gray ellipses for the anode, and blue spheres for the cathode), binders (black strands), and conductive additives that improve the conductivity of the electrode pastes. A porous separator filled with electrolyte is interposed between the electrodes. During discharge, lithium travels out of the anode active material into the electrolyte, crosses the separator, and inserts itself into the positive active material, while electrons flow from the negative active material to the anode collector through an external circuit (not shown) into the cathode collector and to the cathode active material.

Packaging. Since Li-ion cells are extremely sensitive to water and air, their packaging must be hermetic. For small cylindrical cells, nickel-plated steel cans sealed by crimping with gaskets have proven effective. Prismatic cans are usually made of nickel-plated steel or aluminum and sealed by laser welding. Of growing importance is lightweight, flexible battery packaging comprised of layers of polymers and aluminum foil. These flexible packages can provide hermetic seals for many years.

Additives. Numerous additives have been developed to improve battery performance, including carbon nanotubes to improve the electrical conductivity of electrode pastes, functional binders to hold the electrode paste together and provide adhesion to current collectors, and electrolyte additives to improve battery life.

Wrap up

The major challenges that need to be addressed for today's Li-ion batteries are the low voltage of the positive electrode and the limitations of the nonaqueous electrolyte, which is unstable at high and low voltages, has poor transport properties, and is highly flammable. These challenges are being addressed primarily by the development of new materials. For example, ionic liquids and solid electrolytes are being developed as alternatives to organic electrolytes, and additives are being developed to form protective films on electrode surfaces. Process technologies like atomic layer deposition (ALD) are also being explored. Major engineering challenges include the development of improved battery designs that provide higher discharge and charge rates and enable increases in the volume fractions of active materials in the cell.

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LITHIUM-ION BATTERIES

Raw Material Considerations

Gerry M. Clarke, CEng
Minerals Consultant

Among the many elements involved in converting chemical energy into electricity, lithium is currently king. This article looks at the lithium supply picture and the implications of supply and demand on lithium-ion battery technologies and markets.

Although many elements can be used in batteries to store and convert chemical energy into electrical energy, the lithium-ion system dominates today. Various materials have been used or experimented with in lithium-ion battery chemistries, including lithium metal, graphite, aluminum, silicon, lithium titanium oxide ($Li_4Ti_5O_{12}$), and titanium dioxide (TiO_2) for the anode; and titanium sulfide (TiS_2), iron phosphate ($FePO_4$), lithium manganese oxide ($LiMnO_4$), lithium cobalt oxide ($LiCoO_2$), lithium nickel oxide ($LiNiO_2$), and lithium nickel manganese cobalt oxide $Li(NiMnCo)O_2$ for the cathode. Of these, three elements — carbon (in the form of graphite), cobalt, and lithium — have attracted the most attention due to supply concerns based on geological availabilities, geopolitics, and/or market limitations. The other elements have not generated similar interest because the volumes that might be needed for batteries are small relative to availability (Table 1).

Lithium has been the subject of the most discussion, because it is the key ingredient in the lithium-based advanced-battery chemistries, and questions have arisen about supply constraints and the adequacy of lithium resources. Thus, lithium is considered in some detail here so the reader may appreciate why resource adequacy is much less a concern today than previously.

This article explores where lithium is found and in what forms, how much is available, how it is recovered and converted to a form that can be used in batteries, relative operating costs of recovering lithium from different sources — and what all of this means for Li-ion battery makers and users. It also briefly discusses the recovery of carbon and cobalt.

Graphite

The layered crystal structure of graphite provides directional conductivity channels through which lithium ions flow. This makes it an ideal anode material.

Even though carbon is one of the most common elements in nature, it is the form of carbon used for battery applications — primarily natural flake graphite — that has generated supply concern and exploration activity. The U.S. Geological Survey (USGS) estimates world reserves of all forms of graphite to be 77 million m.t., including the more-common, lower-quality amorphous graphite and the rarer, higher-quality lump or vein graphite.

Flake graphite occurs most commonly as a minor constituent in crystalline metamorphic rocks, and is mined mainly in China, India, and Brazil. The USGS estimates that 565,000 m.t. of flake graphite was produced in 2012, of which around 82,500 m.t. was used for batteries.

Following extraction, graphite ore is subject to size reduction and beneficiation by mechanical and froth flotation techniques to separate and concentrate flake graphite to over 85% carbon. For lithium-ion battery applications, this concentrated flake graphite is further purified, typically to over 98–99.95% carbon. Next, it is processed using fine grinding, mechanical fusion, and thermal-chemical techniques to create nearly spherical particles in the 10–40-mm-dia. size range. Then, it is dried, and finally coated with nongraphitic carbon to optimize performance. Japan, China, and South Korea produced over 90% of the world's spherical graphite in 2012.

Supply and demand scenarios through the end of the decade for graphite, particularly of the quality required for

batteries, have spawned exploration and development projects, mainly in Canada, but also in Australia, South Korea, South Africa, Namibia, Mozambique, Tanzania, Sri Lanka, Germany, Czech Republic, Sweden, Norway, and Russia.

Cobalt

Cobalt (in combination with nickel and manganese) is one of the minor metal elements in advanced lithium-ion battery chemistries. Most economically significant cobalt deposits occur in sedimentary copper deposits (in the Congo and extending into Zambia) and large-scale, crystalline igneous rocks rich in magnesium and iron (in Canada, China, and Russia). The USGS estimates that of the 110,000 m.t. of cobalt produced in the world in 2012, 55% was from the Congo and 20% from Russia, China, and Canada.

Although the USGS estimates world cobalt resources to be 15 million m.t., cobalt has a history of being one of the most volatile metals in terms of price fluctuation and, at times, supply constraints. Thus, any large-scale, sustained increase in demand for this material is of potential concern.

Lithium

Lithium is a highly reactive chemical that is not found on Earth in elemental form. Although it is not mined as lithium, the industry uses the name of the element as a convenient shorthand when talking about the array of lithium resources, supply, and demand.

Lithium is the lightest and smallest metallic element. Geochemically, lithium is relatively rare, with a crustal abundance of just 17 ppm (compared with 23,000 ppm for sodium). However, geological processes provide traps for all elements at different stages in the geological evolution of the Earth's crust; this trapping concentrates an element to levels that far exceed its average crustal abundance,

Table 1. World availability of the main advanced-battery raw materials.

Element	Abundance in the Earth's Crust, ppm	Top Three Producers (Market Share of Top Producer)	2012 Production, thousand m.t.	Reserves,* thousand m.t.	Resources,* thousand m.t.	Approximate Cost (for comparative purposes only)
Aluminum	82,000	China (42%), Russia, Canada	44,900	28,000,000†	<75,000,000†	\$0.98/lb
Carbon (as Graphite)	1,800	China (68%), India, Brazil	1,100	77,000	800,000	\$1,530/m.t.
Cobalt	30	Congo (55%), Russia, China	110	7,500	15,000	\$14/lb
Copper	68	Chile (32%), China, Peru	17,000	680,000	>3,000,000	\$3.70/lb
Iron (ore)	63,000	China (43%), Japan, Russia	3,000,000	170,000,000	<800,000,000	\$101/m.t.
Lithium	17	Australia (35%), Chile (35%), China	37	13,000	39,500	>\$6,000/m.t. Li_2CO_3
Manganese	1,100	South Africa (22%), Australia, China	16,000	630,000	Abundant	\$8/m.t.
Nickel	90	Phillippines (16%), Indonesia, Russia	2,100	75,000	130,000	\$17,600/m.t.
Phosphorus (ore)	1,000	China (42%), U.S., Morocco	210,000	67,000,000	>330,000,000	\$100/m.t.
Silicon	270,000	China (66%), Russia, U.S.	7,600	Ample	Abundant	\$1.30/lb
Titanium	6,600	Australia (20%), South Africa, Canada	7,000‡	700,000	>2,000,000	<\$2,250/m.t.
Vanadium	190	China (37%), South Africa, Russia	63	14,000	>63,000	\$6.50/lb V_2O_5
Zinc	79	China (35%), Australia, Peru	13,000	250,000	1,900,000	\$0.86/lb

* Reserves are currently economically feasible and are a subset of resources. Resources are currently or potentially economically feasible.

† World reserves and resources are for the principal aluminum ore, bauxite.

‡ Amount of TiO_2 contained in the titanium ore.

Source: U.S. Geological Survey

enabling it to be economically recovered.

Lithium is found concentrated in older silica-rich igneous intrusive rocks, strata-bound in younger soft sedimentary formations, and in solution in three naturally occurring, but fundamentally different, types of brine. These various forms of lithium have different economics and require different engineering approaches to recovery.

Lithium mineral and chemical resources

Solid, lithium-bearing mineral accumulations in hard igneous rock and liquid lithium-bearing brines trapped in near-surface continental brine aquifers are the two established types of lithium resources. Forecast demand growth has led to the exploration and development of soft sedimentary rock and other brines, which previously were not exploited.

Because lithium chemicals are produced from both mineral (lithium silicates) and brine (lithium chloride) sources, capacities and production volumes are usually expressed in terms of lithium carbonate equivalent (LCE), since Li_2CO_3 is the most common lithium chemical produced from both resource types. While lithium carbonate is the most important lithium chemical sold by brine producers in terms of volume, they also manufacture and sell a host of other derivative lithium chemicals, including lithium hydroxide, lithium chloride, and organo-lithium compounds. Lithium mineral producers have traditionally produced mineral concentrates, of which only a proportion is sold for conversion to lithium chemicals, although this is changing as new mineral projects with integrated plants designed to produce lithium carbonate and lithium hydroxide come onstream.

Mineral sources, being solid, are static and simpler to define and exploit through conventional exploration, mining, and processing techniques. Brine sources, which are liquid mixtures, are mobile and more complex to define, and their exploitation often requires technological innovation.

Continental brines consist of laterally extensive surface or near-surface brine accumulations and are found primarily at high altitudes. Each continental brine resource is unique, with its own complex chemistry that must be carefully managed to ensure that its salts precipitate in the correct sequence and to minimize the loss of desired product in chemical forms that cannot be recovered. Furthermore, each has a unique set of physical characteristics — resource hydrology, porosity, permeability, structure, amenability to accelerated solar concentration, and accessibility — that define a project's technical and economic viability.

Continental brines were first tapped as a source of lithium in Clayton Valley, NV, in 1966. They became the predominant lithium resource a few decades later, after production began at Salar de Atacama in Chile in 1984, Salar de Hombre Muerto in Argentina in 1997, and China's Zhabuye Salt Lake in 2004.

As brine resources were on the rise, mineral production capacity in Australia expanded rapidly, and in recent years the pendulum has swung back to a more even balance in the production from lithium brines (52%) and lithium minerals (48%). With the exception of zabuyelite, the lithium minerals listed in Table 2 have been, or are expected to become, commercially significant sources of lithium. Spodumene is by far the most commonly exploited lithium mineral today.

Lithium sufficiency — myth or reality?

Concern about the lithium industry's ability to serve the growth expected from the advanced-battery sector gained momentum in the early 2000s, as lithium demand in general was already rising, with more-rapid growth in the small-battery sector. This concern arose in part because only three major chemical companies — SQM, Rockwood Lithium, and FMC Lithium — were engaged in lithium production, and it was a small portion of their overall businesses. A fourth producer, Talison Lithium, was a relatively small Australian mining company, and China's activity was not well appreciated.

The fact that the automotive industry might rely on such an apparently restricted supply for even a small fraction of the fleet gave rise to hyperbolic speculation, about which the established lithium industry appeared, at least initially, somewhat complacent. Lithium industry veteran Keith Evans, former chief geologist at Amax Corp., came out of retirement and helped to counter the speculative misinformation through a series of articles and presentations beginning in 2007.

In 2008, Evans referred to a reserve figure of 30 million m.t. of lithium (160 million m.t. LCE) based on a U.S. National Research Council report that had been updated to include all subsequent discoveries since its publication in 1976. The lithium industry, as well as the wider mineral resources industry, began to respond, and a rush to identify more lithium resources took off. In 2012, Evans updated his reserve estimate to 38.89 million m.t. based on the emergence of nearly a hundred new mineral and brine projects.

In contrast to Evans' estimates, most published lithium resource and reserve figures are based on the narrower definitions of deposits as specified by the USGS, Australia's Joint Ore Reserves Committee (JORC), or the Canadian Securities Administrators (CSA). Standards set by these agencies are designed to minimize risks, particularly to third-party investors, in the development of new deposits and to provide reliability and credibility for resource-based asset valuations. Meeting these standards involves rigorous procedures and requires substantial capital, so it was hardly surprising that published reports appeared to suggest resource inadequacies to lithium industry outsiders. It became clear that capitalizing on market growth would require a consensual and objective assessment of broader-based reserves, as contemporary supply-and-demand dynamics were unable

to counter the negative speculation about future supplies. Evans paved the way for this understanding.

Lithium exploration accelerated after 2008, and the number of new projects, including many involving previously untapped types of geological resources, grew to a level that has the potential to outstrip any realistic demand scenario through 2020. However, unless and until more-attractive alternative technologies are identified and implemented, demand for lithium resources of all types will grow in the coming decades, and all technologically feasible projects will likely be called upon at some point to meet that demand. A study by the Ford Motor Co. and the Univ. of Michigan identified demand for elemental lithium of 20 million m.t. over the 90-yr period of 2010–2100. Due to conversion losses, this will require 40 million m.t. of *in situ* resource — very close to Evans' estimates and to this author's own June 2009 estimate of 39.37 million m.t. of reserves.

Today, the lithium industry's focus is less on concerns about lithium resource sufficiency and more on technologies for lithium resource conversion — the bailiwick of chemical engineers. New technologies and efficiency-improvement projects are emerging, the most revolutionary of which (discussed later) remain to be proven on a commercial scale.

While lithium resource development has been dominated by the Americas and Australia, the East Asian nations of South Korea, China, and Japan continue to lead the development of lithium applications technology in the advanced-batteries sector. Although China has lithium resources, it is only now beginning to emerge as a major factor in supply. Furthermore, some corporations with manufacturing operations in Asia are investing in the development of resources in the Americas in order to secure long-term supplies.

Mineral resources

Lithium is found in pegmatites, which are very coarsely crystalline igneous rocks comprised mainly of the light-colored, high-silica minerals of quartz, feldspar, and mica. Pegmatites typically extend in two dimensions and have a thickness of a few to many tens of meters. Because mineralization occurs in several phases, many pegmatites contain zones of symmetrical mineralization on either side of fracture weaknesses. Lower-grade spodumene-bearing pegmatites consist of about 12% spodumene and around 1% Li_2O, while top-grade pegmatites contain 50% spodumene and up to 4% Li_2O. Eucryptite, amblygonite, lepidolite, and petalite also occur in pegmatite host rocks, but

Table 2. Lithium is found in a variety of host minerals and brines. Spodumene and continental brines are the major commercial sources today.

Mineral	Location of Largest Amount	Empirical Formula	Li Content,* %	Li_2O Content,* %
Zabuyelite	China	Li_2CO_3	18.75	40.44
Eucryptite	Zimbabwe	$LiAlSO_4$	5.53	11.84
Amblygonite	Canada	$LiAlPO_4(F,OH)$	4.69	10.10
Spodumene	Australia	$LiAlSi_2O_6$	3.71	8.03
Lepidolite[†]	Zimbabwe	$K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$	3.48	7.70
Jadarite	Serbia	$LiNaB_3SiO_7(OH)$	3.39	7.28
Petalite	Zimbabwe	$LiAlSi_4O_{10}$	2.09	4.50
Zinnwaldite[†]	Czech Republic	$KLiFeAl(Si_3Al)O_{10}(F,OH)_2$	1.58	3.42
Hectorite	United States	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$	0.56	1.17
For Comparison	Earth's Crust	Average 17 ppm	17×10^{-6}	
Liquid	**Location of Largest Amount**	**Li Content**	**Li Content,* %**	
Continental Brine	Chile	<2,700 ppm (with K, B)	0.27	
Oilfield Brine	United States	<700 ppm (with Br)	0.07	
Geothermal Brine	United States	<400 ppm (with Mn, Zn)	0.04	
For Comparison	Seawater	Average 0.18 ppm	18×10^{-8}	

* Theoretical lithium content is expressed in elemental form and conventional oxide form for mineralogical analysis. Actual lithium content will vary according to the degree of elemental substitution within the crystal lattice.

[†] Lepidolite and zinnwaldite are mineral names found in the literature on lithium resources that are no longer recognized as separate mineral species by the International Mineralogical Association, as they are now included within the polylithionite-trilithionite and siderophyllite-polylithionite series, respectively, of phyllosilicate minerals.

are far less commercially significant for the production of lithium than spodumene.

Tin-tungsten-lithium deposits found in the Erzgebirge region of southeast Germany and the Czech Republic (where the lithium mineral is zinnwaldite) are no longer a commercially significant source of lithium. However, with early-stage exploration taking place on both sides of the German-Czech border, these classic deposits may again become an important source of tin, tungsten, lithium, and indium.

Novel soft-rock resources hold considerable promise for meeting future lithium demand. This is a tale of two minerals: hectorite, long-known mainly in the western U.S. and exploited in small volumes; and jadarite, which was discovered in 2006 in Serbia. Both minerals have been identified in large deposits hosted in geologically recent soft, sedimentary-rock basins that may be mined relatively easily by surface and underground methods, respectively. In addition, they may be relatively easily beneficiated to produce mineral concentrate for chemical conversion. However, at this time, they are most significant for extending the known resource base for future lithium exploitation.

Brine resources

Wherever there is brine, there will be dissolved mineral matter, including (in different proportions) such common components as sodium, calcium, magnesium, potassium, boron, chloride, sulfate, and lithium. Although brines containing commercially viable concentrations of lithium are not common, exploration spurred by forecast market demand has been increasingly identifying new sources over the past decade. However, these complex and near-saturated solutions require tight control of phase chemistry to avoid precipitation and loss of lithium as a complex salt and to permit lithium concentration during evaporation.

As recently as 2003, only three continental brine sources had become commercial operations — one each in the U.S. (Nevada), Chile, and Argentina. Now, ten years later, at least three brine operations are at various stages of exploration or operation in China, six in Argentina, two in Chile, and one in Bolivia, and there are several more earlier-stage brine-exploration projects in the western U.S. and South America.

While continental brine resources have common attributes, they are fundamentally different in terms of their key parameters — the most important of which is brine chemistry, *i.e.,* lithium content and the proportions of key components. In addition to securing financing and managing financial risk, the operational challenges in bringing these remote high-altitude projects to fruition are hard to overstate, whether it is brine conversion chemistry, hydrology, raw materials and product logistics, the availability of a skilled workforce, permitting, or product quality assurance.

Two new types of lithium brine resources are emerging — geothermal brines, and oilfield brines. Unlike continental brines, these originate thousands of feet below the surface and have significantly lower lithium content.

Proprietary reverse-osmosis technology has been developed by Simbol Materials to extract lithium from geothermal brines derived from active plate tectonics deep beneath California's Imperial Valley. This brine contains 200–300 ppm lithium. Heat from hot brine (at around 315°C) is the primary resource for geothermal power generation, and cooled brine is the source of dissolved solids from which lithium, manganese, and zinc compounds are recovered. The process offers several advantages over other lithium-recovery methods. It has a small footprint, as it involves no mining. It generates little waste — only very fine silica that must be removed prior to lithium extraction. The process is fast, requiring just 90 minutes to harvest the lithium. And, it produces lithium of high purity, well above today's market requirement of 99.5% Li_2CO_3. The company plans to establish several industrial-scale, 16,000-m.t./yr Li_2CO_3 production facilities, each located at a different geothermal power plant.

In Arkansas, oilfield brines held in highly porous, permeable, deep sedimentary rocks are a major source of bromine. These brines are also a huge lithium resource. Albemarle Corp. announced in 2011 that it had developed new technology to extract lithium from its bromine brine tailings. The process has reportedly been proven on a laboratory scale and a pilot plant is said to exist, but details about the process are not available.

Resource conversion processes

Converting lithium-bearing rock or brine to a saleable product involves three main steps:

- extraction, *i.e.,* mining the mineral or pumping the brine
- concentration by a series of processing stages to remove unwanted material from the mineral ore or liquid brine
- final conversion of the concentrate into the primary lithium chemical product, for sale or for further processing.

The primary product is usually lithium carbonate, from which other lithium chemicals may be manufactured. (An exception to this is the direct conversion of mineral to lithium hydroxide.)

When considering quantitative statements about *in situ* resources and reserves, it is important to appreciate that only a portion survives to saleable product. Losses occur during extraction, beneficiation, and processing. For instance, ore recovery from hard pegmatite by surface operations may be 92%, and ore conversion to lithium carbonate may be 67%. Furthermore, recovery rates vary from deposit to deposit.

Lithium losses from continental brine aquifers are unknown, because none of the aquifers of known volume have yet been drained to the point of technical or economic exhaustion. (However, hydrologists caution that such losses

may be as high as 70%.) No data are available for potential losses from geothermal or oilfield brines.

There are numerous processing routes to lithium carbonate, depending on the characteristics of the resource. A detailed discussion of these routes is beyond the scope of this article, but the following summary demonstrates the complexities involved.

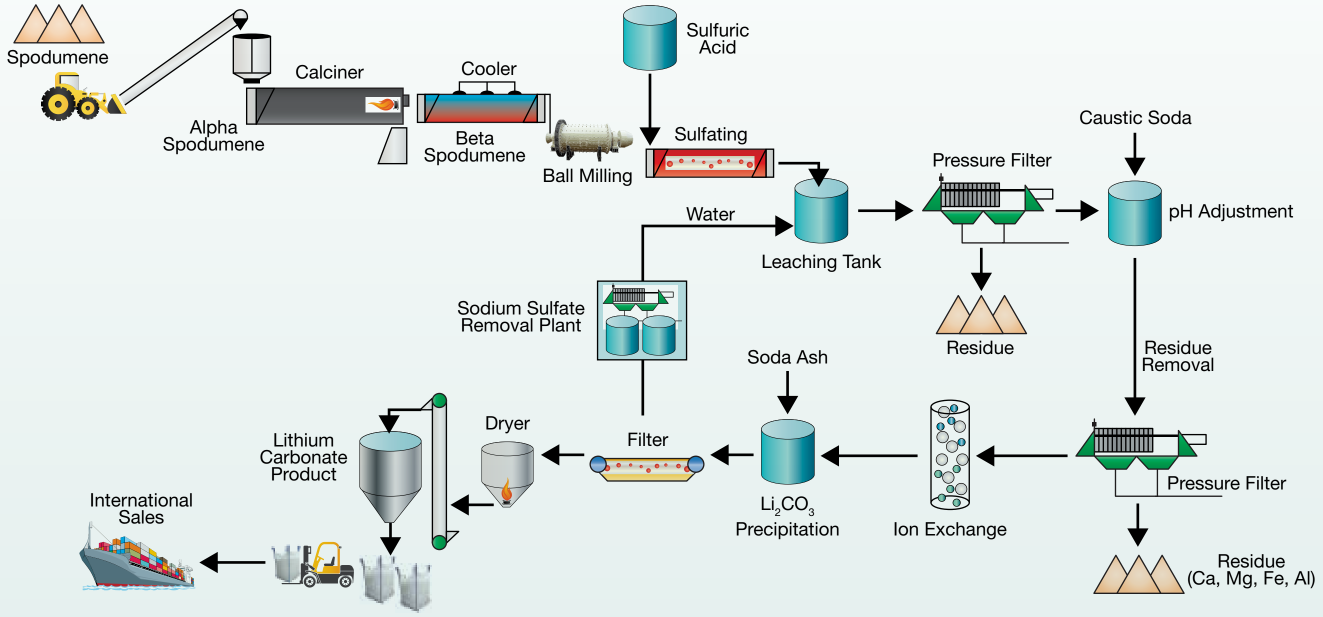
Mineral conversion

Conventional open-pit mining involves drilling, blasting, and hauling the ore to a beneficiation plant. There, the ore feed is crushed, ground, screened, and sorted, and then the desired minerals are separated from the unwanted rock components. Separation by gravity, dense media, froth flotation, and/or magnetic techniques in a continuous-flow process concentrates the desired mineral. In this way, spodumene ores are concentrated from around 1% Li_2O in the ground to 6% Li_2O in the mineral concentrate, which is sold for direct use (*e.g.,* in ceramics and glass) or converted to lithium chemicals.

The world's first continuous-process plant for converting spodumene concentrates to lithium carbonate (Figure 1) was commissioned in 2012 in China by Galaxy Resources. Spodumene concentrate is first calcined at 1,070–1,090°C to convert natural α-spodumene to β-spodumene, which renders the mineral acid reactive. The granular mix of β-spodumene and unwanted minerals is cooled to about 100°C and dry-ground to particles with diameters less than 200 μm, then mixed with concentrated sulfuric acid and fed to the sulfating kiln. From there, the dry material is gravity-fed to a tank, where it is leached with spent liquor and make-up water. Optimum pulp density is maintained to maximize lithium concentration at the crystallization stage and to ensure that the solubility limit of lithium sulfate is not exceeded during leaching. The resulting lithium sulfate and residual slurry exiting the leach tank is thickened and filtered to remove unwanted solids from the process liquor. A filtration and thickening circuit removes the residue, which contains calcium, magnesium, iron, and aluminum, from the lithium sulfate solution. The solution is filtered and then reacted with soda ash (Na_2CO_3) to crystallize lithium carbonate. The lithium carbonate is thickened and the crystals are allowed to settle, then they are separated from the spent liquor, filtered, dried, and stored. The process solution is evaporated to crystallize byproduct sodium sulfate. The resulting lithium carbonate has a grade of >99.5% Li_2CO_3.

A proprietary process that uses electrolysis to make high-purity lithium hydroxide and lithium carbonate (Figure 2) has been developed by Nemaska Lithium for its plant in Quebec. Lithium sulfate is first produced from spodumene concentrate containing 6% Li_2O, and the lithum sulfate is then transformed by electrolysis into liquid lithium hydroxide. The lithium hydroxide is then converted to the solid monohydrate form or bubbled with carbon dioxide to form lithium carbonate. The main cost is for electricity, which in Quebec is supplied by highly predictable and cost-effective hydroelectric generation. The electrolysis technology avoids the need for soda ash, a reagent used in traditional carbonate manufacturing methods that is subject to wide price swings.

Hectorite and jadarite resources have not yet been commercialized, although processes to convert them to lithium



▲ **Figure 1.** This continuous process makes lithium carbonate from spodumene. Source: www.galaxyresources.com.au/project_jiangsu.shtml.

carbonate have been developed.

Hectorite. Near-surface hectorite clay is easily recovered by bulk open-pit extraction methods, and beneficiation requires only size reduction before the ore is blended with anhydrite, gypsum, and calcium carbonate to form 2–5-mm-dia. granules. Calcination of the granules at 1,050°C and leaching with recycled liquor at 70–90°C yields a brine composed of dissolved lithium, potassium, and sodium sulfates and a solid residue that is filtered and discarded as tailings. Further evaporation of the brine crystallizes potassium sodium sulfate, potassium sulfate, and sodium sulfate, leaving enriched lithium sulfate brine that is then reacted with soda ash to recover lithium carbonate.

Jadarite. Because jadarite ore lies deep below the surface, underground room-and-pillar mining is envisaged for its extraction. Beneficiation of the largely free-milling ore, mainly by wet scrubbing techniques, yields a concentrate that is subjected to hot sulfuric acid digestion, waste removal by leaching, boric acid crystallization, magnesium and calcium removal from the boric acid liquor by precipitation with lime, precipitation of lithium carbonate by the addition of soda ash, and crystallization of sodium sulfate from the lithium carbonate liquor. For each metric ton of lithium carbonate, 4.5 m.t. of boric acid is required.

Continental brine conversion

Even though the principle of sequential solar evaporation of pumped brine in laterally extensive ponds is simple, the details of the process are complex. Many variables related to aquifer hydrology (porosity, permeability, flowrates, and brine area, depth, and composition) and meteorology (temperature, humidity, wind velocity and direction, rainfall, and insolation) need to be optimized to achieve the correct well-pumping rates and sequential precipitation. Key composition parameters are the ratios of other elements to lithium (*e.g.*, Mg:Li). As these ratios increase, so do processing costs for separating the materials by fractional crystallization or selective precipitation.

Each brine field has distinctive characteristics, so process flowsheets must be tailored to each one. In principle, the process involves multi-well pumping of brine from carefully selected positions at depths of 30 m to as much as 900 m to a series of lined evaporation ponds. These ponds may extend up to 25 km^2 depending on the brine's characteristics and requirements for recovering potash as a coproduct. Evaporation causes the sequential precipitation of sodium, magnesium, and potassium salts, which require regular removal to maintain the correct working pond volume.

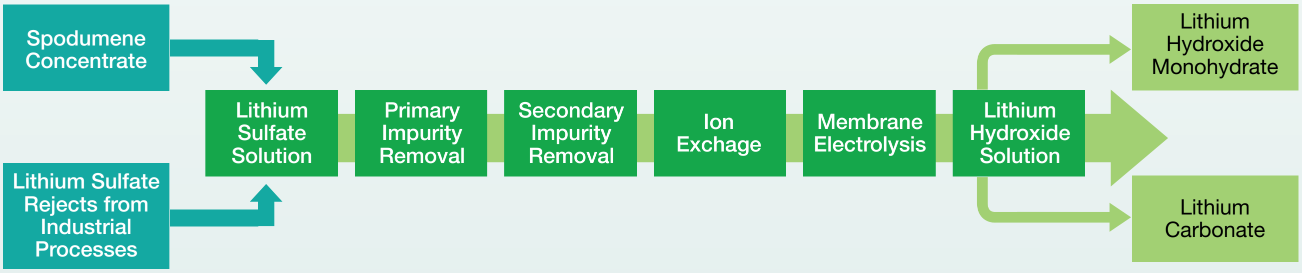
Depending on the original brine's composition and lithium concentration, under favorable meteorological conditions, it takes 12–18 months to obtain the maximum concentration of lithium chloride (38% LiCl, 6% Li) before precipitation of undesirable salts occurs. The lithium chloride is then removed and purified, and the remaining magnesium and sulfate impurities are removed along with boron, which may be recovered as a coproduct. The purified lithium chloride solution is treated with soda ash to precipitate lithium carbonate, which is then filtered, dried, and stored in bags. Refined lithium chloride and lithium hydroxide may also be produced.

The Salar de Hombre Muerto facility preconcentrates the lithium via selective adsorption onto hydrated alumina. Residual brine is returned to the aquifer. The adsorption columns are washed to yield a lithium chloride solution containing up to 1% Li (a concentration factor of around 20). This solution is further concentrated by solar evaporation and reclaimed for processing to lithium carbonate. The hydrated alumina adsorption columns are regenerated for another lithium adsorption cycle.

At other projects, evaporation ponds raise the brine's lithium chloride content to 2.5 g/L, then hydrated lime and sodium sulfate are added to precipitate magnesium hydroxide and calcium sulfate. A second stage of solar evaporation raises the lithium concentration to chemical plant feed grade.

Earlier this year, South Korean steelmaker POSCO announced a potentially revolutionary modular process for:

- sequential recovery of calcium and magnesium cake, and the subsequent separation and production of magnesia (98.9% MgO) and calcium carbonate (99.2% $CaCO_3$)
- extraction of a primary lithium compound from the magnesium- and calcium-depleted brine and manufacture of lithium carbonate (99.9% Li_2CO_3) and lithium hydroxide (99.62% LiOH)



▲ **Figure 2.** A proprietary electrolysis process makes lithium carbonate and lithium hydroxide from spodumene.
Source: http://www.nemaskalithium.com/en/plant/process

- evaporation of the lithium-depleted brine and recovery of potassium chloride (99.62% KCl) by flotation
- production of borax (99.9% $Na_2B_4O_7 \cdot 10H_2O$).

The process does not rely on solar evaporation. Total production time for lithium products is less than a month, with the lithium process module requiring just eight hours. A minimum recovery rate of 80% is claimed based on pilot plant work. Another advantage of the process is a much smaller operational footprint.

Operating costs

The production of lithium carbonate from continental brines has generally been less expensive than from hard rock sources.

Operating costs (in U.S. dollars) for brine facilities are reportedly in the range of $1,550–2,000/m.t. in Chile, $2,600/m.t. in Argentina, and around $3,100/m.t. in China. Three brine projects that are going through financing and starting construction in Argentina are expected to have net operating costs in the range of $1,332–2,200/m.t.

Operating costs for producing lithium carbonate from hard rock pegmatite resources in Australia have been estimated at up to $4,538/m.t., and $4,700/m.t. in China. Costs for new projects in Canada are estimated to be lower, at $3,164–3,500/m.t., or $2,350/m.t. net after byproduct credits. For lithium carbonate production from hectorite clay in Nevada, operating costs have been estimated at $3,472/m.t., and just $968/m.t. after byproduct credits.

Lithium supply and demand scenarios

The USGS estimates that world lithium production in 2012 was 196,951 m.t. LCE. Consumption lagged by about 27%, at around 144,000 m.t. LCE, up by approximately 9% over 2011 consumption.

Lithium project development continues apace, with a somewhat competitive dimension to the march through preliminary economic assessment (PEA), feasibility study (FS), financing, and construction to commissioning. Five continental brine projects in Argentina, three projects in the U.S. involving geothermal brine, oilfield brine, and hectorite, and nine spodumene projects across Australia, Austria, Canada, and China are at or beyond the PEA stage, with the goal of beginning production in 2015 or sooner. Demand in Asia Pacific countries is also driving resource development. China's domestic resources, however, continue to underperform, and mineral conversion capacity is expected to expand, outstripping current production levels, after 2014. Dozens of exploration projects, mainly in North America but also in Europe, are underway as well.

Table 3 presents aggregated demand scenarios derived from forecasts made in recent years by various analysts using compound average annual growth rates of 9–10%. One forecaster's earlier demand estimate of 500,000 m.t./yr LCE by 2020 is now regarded as more likely to be realized in 2025.

Based on the demand forecasts of 9–10% through 2020 shown in Table 3, combined with current producer capacity and recent expansions, and new projects that are in the planning through startup phases (Table 4), a supply overshoot scenario appears likely (Table 5).

Table 3. Aggregated lithium demand forecast.

	Forecast Demand, m.t./yr LCE	
	2015	2020
Bullish Case	265,000	300,000
Average Case	191,500	237,400
Conservative Case	138,500	174,800

Table 4. Producer capacity and forecast demand.

	Forecast, m.t./yr LCE	
	2015	2020
Combined Producer Capacity*	231,000	251,000
Excess (Shortfall) Relative to Bullish Case	(34,000)	(49,000)
Excess (Shortfall) Relative to Average Case	39,500	13,600
Excess (Shortfall) Relative to Conservative Case	92,500	76,200

* Current and projected capacity for four established producers: SQM, Rockwood Lithium, FMC Lithium, and Talison Lithium.

Table 5. Producer capacity combined with capacities of advanced projects compared with forecast demand.

	Forecast, m.t./yr LCE	
	2015	2020
Combined Producer Capacity*	231,000	251,000
Capacities of Advanced Projects Currently Underway†	58,750	92,000
Total Combined Producer Capacity	289,750	343,000
Excess (Shortfall) Relative to Bullish Case	24,750	43,000
Excess (Shortfall) Relative to Average Case	98,300	105,600
Excess (Shortfall) Relative to Conservative Case	151,250	168,200

* Current and projected capacity for four established producers: SQM, Rockwood Lithium, FMC Lithium, and Talison Lithium.

† Six advanced projects by ADY Resources, Canada Lithium, Galaxy Resources, Lithium Americas, Orocobre, and Simbol Materials. Supply from other resources in China and elsewhere are not included.

Article continues on next page

A significant factor in the supply-and-demand picture is installed capacity utilization, and whether, and to what extent, this may be able to increase above recent levels of 60% before new capacity is required to ease potential supply constraints.

Based on the installed capacity-utilization levels in Table 4, the excess capacity of 13,600 m.t./yr LCE in 2020 being just 6% above the average demand forecast of 237,400 m.t./yr LCE, and shortfalls relative to the bullish-case forecasts in both 2015 (13%) and 2020 (16%), and assuming that all expansion plans of established producers are realized, there appears to be room for three or four new projects. A compound average annual growth rate of 9% corresponds to the average forecast of 191,500 m.t./yr LCE for 2015; by 2020, the same 9% growth rate leads to a demand of about 288,000 m.t./yr LCE — roughly 20% higher than the capacity forecast of 237,400 m.t./yr LCE.

To sustain more than three or four new projects through the forecast period, an uptick in demand growth from the developing advanced-battery markets (*e.g.,* automotive, electricity grid storage, electric bicycles) seems to be necessary. The likely prognosis, however, is that many projects, particularly those in the earlier planning stages, will be put on hold until demand can support them, probably beyond 2020 and through 2025.

A comparison of current installed capacities and known expansions of the four major lithium producers with the 2020 demand scenarios (Table 4) reveals:

- a significant shortfall in the bullish case
- very tight supply in the average case
- oversupply in the conservative case.

The bullish and average forecasts combined with the capacity-utilization estimates for current producers have fueled the race for new projects to come onstream.

Table 5 adds six projects that have been announced to the capacities of the four established producers. The total of the projected capacities significantly exceeds the forecast demand in all three scenarios — indicating the potential for substantial oversupply.

These supply-and-demand scenarios illustrate the situation today. But, demand and the supply project mix will likely change tomorrow. For example, in addition to the plants and projects reflected in Tables 4 and 5, activity in China will also impact supply and demand. Five continental brine operations and expansions have as-yet-unfulfilled potential for significant Li_2CO_3 output, at least one major spodumene mine and plant is under construction, and mineral conversion enterprises continue to expand to meet China's insatiable appetite for lithium feedstocks. And, Bolivia is hopeful about overcoming significant technical challenges at Salar de Uyuni, with help from South Korea, to reach the plant's full capacity of 30,000 m.t./yr Li_2CO_3 in 2015.

By 2015, demand from China's battery sector alone is forecast to be 35,000 m.t. Li_2CO_3, according to Sichuan Tianqi Lithium Industries Vice President Vivian Wu. Of that, about 34% is for small batteries for computers and portable electronic devices, and the balance is for larger batteries. Growth rates are stunning, as the forecast is almost nine times the 2011 demand of just under 4,000 m.t. and double the 2014 forecast of around 17,500 m.t. Demand for Li_2CO_3 for the production of large batteries is forecast to overtake consumption for smaller batteries in 2014, before accelerating to about two-thirds of total demand in 2015. The main driver for the accelerating lithium demand for large batteries is the electric bicycle, which is forecast to account for 55% of large-battery lithium consumption in 2015. Growth rates for other uses, such as automotive, energy storage, base stations, and power tool applications, are also impressive.

Closing thoughts

The prognosis for lithium supply and demand over the coming decades will be determined by market forces and technology development rather than by any natural availability constraint of Earth's resources. In the shorter term (through 2025), the lithium resource development scenario is more akin to a well-stocked larder, with many lithium resource projects lining up. Depletion and additional resource discovery and development could very well accelerate significantly when, and if, large-scale electricity grid storage and vehicle electrification take off.

Long-term demand will require chemical (and mineral) engineers to continue developing solutions for the economic recovery of lithium from a diverse natural resource base. CEP

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LITHIUM-ION BATTERIES
Component Materials

Avani Patel
Dow Energy Materials

The materials used in the construction of a battery's components must be chosen carefully to optimize battery performance for the specific application.

The lithium-ion battery is an incredibly complex batch reactor, with solids, liquids, and gases reacting in a system that combines organic and inorganic chemistry, heterogeneous catalysis, and electronic physics. Yet, despite its complexity, this reactor is expected to cycle reversibly hundreds or perhaps thousands of times.

It is important to recognize that the lithium-ion battery is a system, where all components and interactions between components affect the performance of the battery, and in turn the performance of the device it powers. The materials used in the construction of the battery's components vary significantly by application. And these materials must be carefully chosen to ensure that the characteristics of the operating battery are consistent with the expectations of the user. Table 1 summarizes the most common materials for the battery's main components — the cathode, anode, electrolyte, and separator.

Because lithium-ion batteries are used across a wide range of applications, cell manufacturers must choose materials that perform best on the metrics that are most important for the application. The key attributes that must be considered regardless of the application are: energy density, power density, safety, lifetime, and cost. Figure 1 shows the impacts of material choices on these metrics.

The energy density of the battery governs the amount of electricity that can be delivered by a battery of a specific size. For automotive applications, more energy allows the vehicle to go farther on a single charge. In general, the cathode has a large effect on energy density because the choice of cathode material determines the capacity (lithium content) of the battery and contributes to the operating voltage.

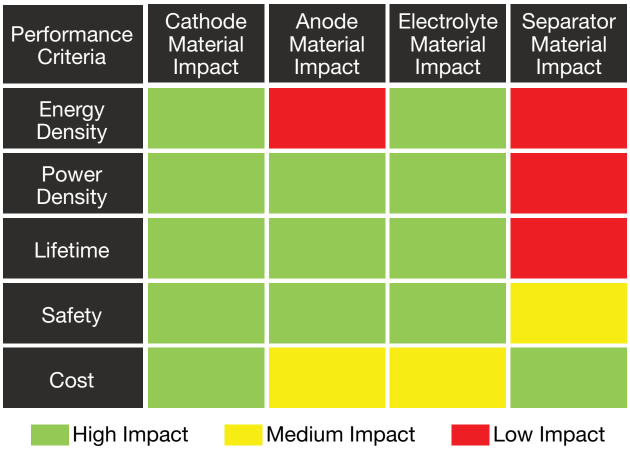
Power density refers to the rate at which the battery delivers current. As a battery discharges during use, lithium ions move out of the anode into the electrolyte, across the separator, and back into the cathode at the opposite terminal. The rate at which these processes occur throttles the power of the cell. As a result, the electrolyte materials and the electrode (anode and cathode) materials are all important choices when tuning the power of the battery design.

Many components influence battery lifetime, some dramatically. This is because a battery can fail by various mechanisms, including mechanical stresses on the electrode materials during cycling, dissolution of cathode materials in the electrolyte, and reactions between the electrolyte and the cathode and anode surfaces.

Battery safety concerns center primarily on the thermal

Table 1. Major components of a lithium-ion battery and their purpose.

Component	Common Materials	Purpose
Cathode	$LiCoO_2$, $LiNi_xMn_yCo_{1-x-y}O_2$, $LiNi_xCo_yAl_zO_2$, $LiMn_2O_4$, $LiFePO_4$	Source of lithium ions Stores lithium ions in the discharged state Operating voltage is determined by the cathode/anode combination
Anode	Graphite, $Li_2Ti_5O_{12}$	Stores lithium ions in the charged state Operating voltage is determined by the cathode/anode combination
Electrolyte	Carbonate solvents with $LiPF_6$ salt and performance additives	Means for lithium ions to move back and forth in the battery
Separator	Polypropylene, Polyethylene	Physically separates the anode from the cathode



Performance Criteria	Cathode Material Impact	Anode Material Impact	Electrolyte Material Impact	Separator Material Impact
Energy Density	🟩	🟥	🟩	🟥
Power Density	🟩	🟩	🟩	🟥
Lifetime	🟩	🟩	🟩	🟥
Safety	🟩	🟩	🟩	🟨
Cost	🟩	🟨	🟨	🟩

🟩 High Impact 🟨 Medium Impact 🟥 Low Impact

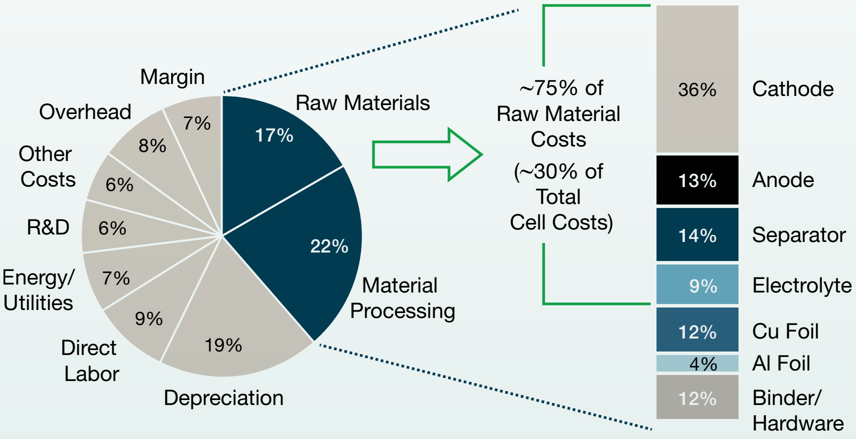
▲ **Figure 1.** The material selected for each battery component can influence critical performance metrics.

instability of the electrode materials. At high operating temperatures, degradation products that can react with the flammable organic electrolytes may form.

As shown in Figure 2, the raw materials and their processing account for about 40% of a cell's cost, and about 75% of that (roughly a third of the total cell cost) is for the four main components. The cathode materials account for the largest portion of the materials cost due to high raw materials costs (*e.g.,* for Ni and Co), as well as high processing costs for upgrading the metals from ore into useful forms.

Cathode materials

To create the positive electrode — which releases lithium ions during charging and accepts ions during discharging (use) — a cathode material is applied as a coating on a current collector (*e.g.,* aluminum foil). In general, the choice of cathode material determines many of the performance characteristics of the battery.



▲ **Figure 2.** The cathode accounts for the largest portion of a cell's material costs. Source: Roland Berger Strategy Consultants, presentation at Batteries 2011.

Olivine materials, such as lithium iron phosphate (LiFePO$_4$, or LFP), allow lithium diffusion in only one dimension. Therefore, they are structurally stable and very safe. LFP has a relatively low lithium density and operates at a relatively low voltage; thus, significant research effort has been focused on improving the energy density of the LFP. An industrially relevant alternative to LFP is lithium manganese iron phosphate (LiMn$_x$Fe$_{1-x}$PO$_4$, or LMFP), which has higher energy density than LFP because manganese operates at a higher voltage than iron.

On the other hand, spinel materials, such as lithium manganese oxide spinel (LiMn$_2$O$_4$, or LMO), allow lithium to diffuse across three dimensions. As a result, the flux of lithium ions out of the cathode material can be very high. Spinels offer some of the highest charge and discharge rate capabilities among cathode choices, although they generally have a lower capacity than olivine-based chemistries.

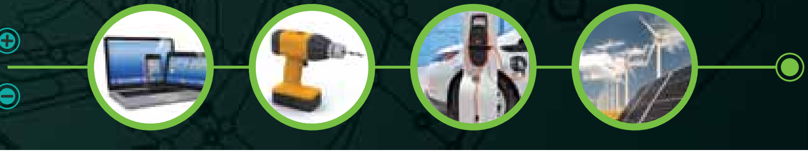
Layered materials, such as lithium cobalt oxide (LiCoO$_2$, or LCO) are commercially mature and represent a good balance between theoretical capacity and rate capability. However, the material begins to collapse if more than 50% of the lithium atoms are removed from the cathode during the charging cycle. Thus, the useable capacity of layered materials is often much lower than the theoretical limit.

For this reason, newer alternatives, such as lithium nickel manganese cobalt oxide (LiNi$_x$Mn$_y$Co$_{1-x-y}$O$_2$, or LNMC), that provide better access to the available lithium have been developed. Over the last few years, LNMC's share of the lithium-ion battery market has increased, primarily for use in notebook PCs, due to its improved safety over that of LCO.

Lithium-ion batteries are unique among commercialized redox battery chemistries because cathode material choices can be tuned to the application. For instance, the automotive industry is interested in ultrasafe materials that can be cycled thousands of times. Manufacturers of portable electronic devices, on the other hand, prefer high energy density but are content with far fewer cycles, since many users upgrade their devices before the batteries have undergone even a thousand cycles.

As shown in Figure 1, all cathode materials require sacrifice on some metrics in order to maximize performance in other areas. As a result, significant R&D is underway to address unmet market needs. Table 2 highlights the strengths and weaknesses of the major cathode materials, all of which have room for improvement in one or more areas.

Lithium-rich (also referred to as



layered-layered, or overlithiated) nickel manganese cobalt oxide (xLi_2MnO_3•$(1–x)LiMO_2$, or LLNMC), lithium nickel manganese oxide spinel ($LiNi_{1/2}Mn_{3/2}O_4$, or LNMO), and lithium cobalt phosphate ($LiCoPO_4$, or LCP) appear to be good materials for next-generation lithium-ion batteries because they offer the promise of higher energy densities and higher operating voltages. Due to structural instability and unintended electrolyte decomposition, cycle life can be a challenge with these materials. However, their redox chemistries take advantage of high-voltage redox potentials, and cells made with these materials can be designed with much higher energy densities. For instance, materials such as LLNMC charged to 4.6 V have been shown to have gravimetric energy densities approaching 1 kWh/kg, almost twice the energy density of the incumbent LCO (570 Wh/kg at 4.3 V).

Nevertheless, since the cell's energy density is directly proportional to the operating voltage, these materials will require electrolytes that are stable above the typical 4.2 V if they are to operate for many cycles. Otherwise, electrolyte decomposition at high voltage can prematurely deactivate the battery.

Anode materials

To make the negative electrode, the anode material is deposited as a coating on copper foil. The anode accepts lithium ions during charging and releases ions during discharge. The anode material also impacts energy, power, safety, and cycle life.

The difference between the operating potential of the cathode and the operating potential of the anode determines the overall potential of the cell. Therefore, the choice of anode paired with the cathode material can have a significant impact on the amount of energy the cell provides.

Furthermore, the capacity of the anode must be balanced against the capacity of the cathode — that is, when lithium ions are transferred from the cathode to the anode during charging, there must be enough room in the anode to accept all of the lithium. Anode materials with higher gravimetric capacity allow for less actual material to be used in the battery, making the cell lighter, smaller, and more desirable to consumers.

Anode material choice can also impact safety. If the anode material is unable to accept lithium ions fast enough, instead of intercalating into the anode, the ions can react on the surface to form lithium metal dendrites. These dendrites can grow like needles inside the cell and often lead to premature deactivation and, more rarely, shorting of the cell. Thus, the choice of anode material is very important.

It is common to choose the anode material based on the material used for the cell's cathode. For this reason, many battery material suppliers offer products that optimize the anode material based on the cathode.

The most common anode material is carbon, specifically in the form of graphite, and both natural and synthetic options are available. Graphite is desirable because of both its low cost and its low operating voltage. While its capacity of about 370 mAh/g is respectable compared to that of most cathode materials, its operating voltage is only 0.1 V vs. Li^0. (Li^0 is arbitrarily defined by the industry as 0.0 V because reducing Li^+ to Li^0 on lithium metal is a well-defined reference system.) Thus, very little voltage penalty is paid by the cell designer when graphite is used as the anode material. Nevertheless, as cathode materials with increasingly higher capacities (such as LLNMC, at 250 mAh/g), are introduced, there will be pressure to improve the capacity of anode materials.

Another anode material being tested in the marketplace is lithium titanate ($Li_{4/3}Ti_{5/3}O_4$, or LTO). The theoretical capacity of the LTO anode is approximately 170 mAh/g, about half that of graphite, and LTO operates at 1.5 V vs. Li^0. Even though the operating range is not as wide as graphite's and the capacity is lower, the higher anode potential prevents metallic lithium deposition and dendrite formation, so cells made with LTO anodes are safer. Furthermore, LTO anodes have been shown to have a longer cycle life than that of graphite because LTO experiences almost no crystal lattice volume change during the charge and discharge processes. Due largely to the improved cycle performance and cell safety, LTO is generally considered when safety and reliability are more critical than the capacity and operating

Table 2. Cathode material performance characteristics relative to key design metrics.

Cathode	Gravimetric Energy Density, Wh/kg*	Power	Cycle Life	Safety	Price, $/kg
LFP ($LiFePO_4$)	500 (3.8 V)	+	+	+	15–22
LMFP ($LiMn_xFe_{1–x}PO_4$)	570 (4.3 V)	+	0	+	15–22
LMO ($LiMn_2O_4$)	480 (4.3 V)	+	0	+	12–15
LCO ($LiCoO_2$)	570 (4.3 V)	+	+	0	30–70
LNMC ($LiNi_xMn_yCo_{1–x–y}O_2$)	570–690 (4.3 V)	0	0	–	20–50
LLNMC (xLi_2MnO_3•$(1–x)LiMO_2$)	960 (4.6 V)	–	–	0	20–40
LNMO ($LiNi_{1/2}Mn_{3/2}O_4$)	630 (5.0 V)	+	0	0	15–25
LCP ($LiCoPO_4$)	720 (5.0 V)	+	0	0	20–50

* Values in parentheses are charge voltage vs. Li^0.

Key: (+) Clear strength, (–) Clear improvement opportunity, (0) Neither a strength nor weakness

Table 3. Typical properties of battery separators.

Property	Typical Value
Thickness	20–25 µm
Porosity	40–50%
Average Pore Size	<0.1 µm
Gurley Number*	200–600 s/100 cm^3 air
Tensile Strength	150–2,000 kg/cm^2
Puncture Strength	300 g/25.4 µm
Thermal Shrinkage at 90°C over 1 h	0–10%

* The Gurley number is the time required for 100 cm^3 of air to pass through 1 $in.^2$ of a material at a pressure differential of 4.88 in.H_2O.

voltage of the cell — for instance, stationary energy storage, where safe and reliable grid storage is preferable to small, light, portable batteries.

The lithium-ion battery industry is devoting a significant amount of R&D to looking for alternative anode materials with higher energy densities. Both silicon- and tin-based anode systems are attractive in this regard. While they offer much higher capacities than graphite materials (silicon has a theoretical capacity of about 4,200 mAh/g), the volume expansion (400%) on charging is a huge technical challenge for designers using this material. While there are several research programs devoted to stabilizing silicon-based anodes, their solutions have seen success only at the R&D scale and an economically viable solution is still lacking.

Electrolyte formulations

Formulated electrolytes are typically liquid solutions of lithium salts that enable the transfer of lithium ions between the cathode and the anode. Electrolyte formulations consist of a mixture of aprotic solvents (which neither accept nor donate hydrogen ions), such as ethylene carbonate (EC) and dimethyl carbonate (DMC); lithium salts, such as lithium hexafluorophosphate ($LiPF_6$); and specialized additives that fine-tune the performance to meet the needs of the application.

Electrolyte formulation varies based on the other components within the cell, cell design, and targeted application. For example, the low operating voltage of graphite-anode cells causes the reduction of carbonate electrolyte solvents on the anode surface to create a solid-electrolyte interface (SEI). So, the electrolyte formulations for these cells generally include an additive that improves SEI formation and provides electrolyte stability.

Due to their highly customized nature, electrolyte formulations are manufactured in small batches, and the formulations are fine-tuned with functional additives based on the user's needs. The formulation technology is knowledge-intensive, and additives are protected as intellectual property.

Carbonate-based electrolytes are not stable at voltages higher than about 4.2 V vs. Li^0. However, cathode chemistries being developed in the lab today operate at voltages ranging from 4.6 V to 5.0 V. The success of these cathode technologies will depend on the development of stable next-generation high-voltage electrolytes. These electrolytes will need to have reductive stability on par with that of current electrolytes, but oxidative stability that extends to the new cathode operating voltage.

Separator

A battery separator is a porous, electronically insulating film placed between the anode and the cathode of the battery. The separator is soaked with the electrolyte, which occupies the pores in the film. This allows ionic transport between the electrodes via the electrolyte while preventing direct electrical contact between the anode and cathode.

The most common type of lithium-ion battery separator is a microporous polyolefin film. Separators are typically made of polypropylene (PP), which maintains dimensional integrity at high temperatures, or polyethylene (PE), which softens at a lower temperature, stopping ion transport and preventing thermal runaway. Three-layer separators of polyethylene sandwiched between polypropylene (PP-PE-PP) combine the advantages of the two materials.

Table 3 lists the properties of lithium-ion battery separators that factor into separator design: low thickness to maximize the space in the battery devoted to active materials; good mechanical properties to prevent shorting during manufacture and operation; and good flow properties to facilitate ion transport.

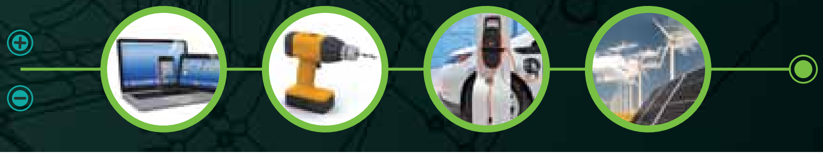
Recent development efforts in the separator industry are focused on a continual push toward reduced thickness, and coatings that enhance high-temperature dimensional stability.

The path forward

Components can be combined in a variety of ways to tune the cell's performance for the intended application. Optimization of the battery system by appropriate pairing of key materials can significantly impact battery performance.

Researchers are working to develop next-generation materials for cathodes, anodes, and electrolytes, and targeting 50–100% improvement in energy density. In electric vehicle applications, this would translate to extended driving range.

Beyond lithium-ion batteries, academia and industry are looking at lithium-air and lithium-sulfur batteries, as well as flow batteries and magnesium intercalation batteries. The U.S. Dept. of Energy recently established the Joint Center for Energy Storage Research, led by Argonne National Laboratory, to explore these and other options.



LITHIUM-ION BATTERIES

Endless Uses

Andrew N. Jansen
Argonne National Laboratory

Lithium-ion batteries can be tailored to suit a range of products in almost any industry. This article describes the main applications for which these batteries are used, and explores some of the challenges hindering future advances.

Batteries have often been derided since their invention over two centuries ago. Thomas Edison stated in 1883, "The storage battery is, in my opinion, a catchpenny, a sensation, a mechanism for swindling the public by stock companies. The storage battery is one of those peculiar things which appeals to the imagination, and no more perfect thing could be desired by stock swindlers than that very selfsame thing. ... Just as soon as a man gets working on the secondary battery it brings out his latent capacity for lying. ... Scientifically, storage is all right, but, commercially, as absolute a failure as one can imagine."

Those are harsh words, considering that in 2012 the battery industry reached $100 billion in sales worldwide, of which $12 billion was in lithium-ion batteries.

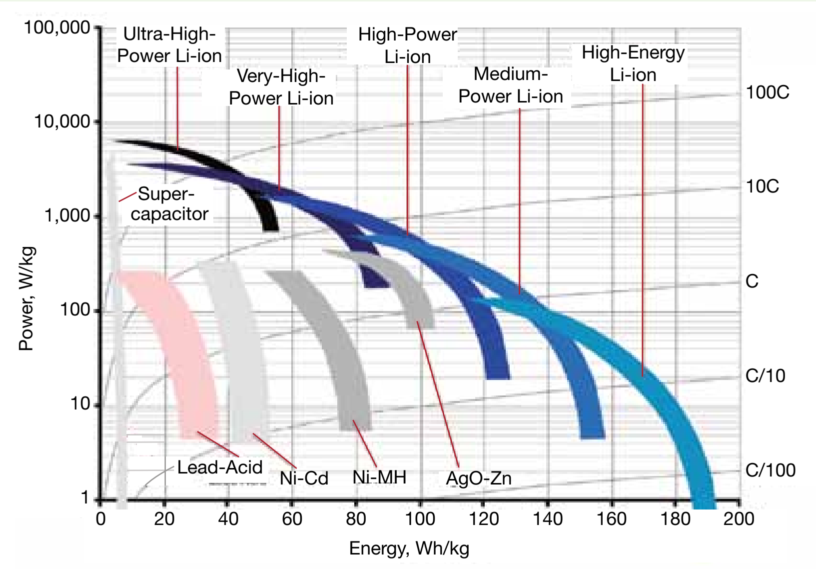
There are several reasons why batteries are maligned by the general consumer — one of which is a misunderstanding about what creates energy in a battery. The term itself, battery, is a very generic term that refers to a group of cells that convert chemical energy into electrical energy to produce a direct current. But, where does this chemical energy come from?

Any pairing of an oxidant and reductant can create chemical energy, which can be harnessed in a battery under the right circumstances. The aqueous battery market includes chemical pairings such as zinc/manganese oxide, nickel/cadmium, nickel/metal hydride, nickel/iron, lead/lead oxide, zinc/air, zinc/mercuric oxide, and zinc/silver oxide, among others. The nonaqueous lithium-ion battery market commonly pairs graphite or carbon as the negative electrode with a variety of lithiated transition metal oxides as the positive electrode. Each pairing represents a chemical reaction with unique conditions and properties that must be respected to achieve the desired performance.

While aqueous batteries can be primary (*i.e.,* single-use) or secondary (*i.e.,* rechargeable) depending on the chemical pairing and design, essentially all lithium-ion batteries are designed to be rechargeable. Lithium-metal batteries, which contain lithium metal or a lithium metal alloy as the negative electrode, are usually primary batteries.

Another common complaint regarding batteries is the problem of short lifespan. Textbooks typically show the electrochemical reaction within a battery as a simple balanced reaction — which is usually far from the actual condition within a commercial battery. It is better to think of battery chemistry as a corrosion reaction, and in the case of rechargeable batteries, a corrosion reaction that must run forward and backward hundreds to thousands of times. Small defects and impurities (at the ppm level) can drastically shorten the calendar life of any rechargeable battery, including lithium-ion batteries. Side reactions are always a concern in rechargeable batteries, as they lead to inefficiencies in capacity and energy, in addition to self-discharge. However, many of these side reactions are necessary evils within the battery system, and they are often required to form a passivation layer on the electrodes to prevent breakdown of the electrolyte. Operating a battery outside of its normal operating temperature range or voltage window, or exceeding its power rating, can have a significant effect on these side reactions and thus impact cycle, calendar, and shelf life.

The most important point that battery consumers need to remember is that battery chemistries and designs are tailored to their intended applications. This is just as true for lithium-ion batteries as it is for aqueous batteries. Some batteries are designed for high energy, some for high power, some for long life (cycle, calendar, or shelf), some for enhanced safety, and some for low cost. No battery system does it all in one package, and any salesperson who promises it all has tapped into his or her "latent capacity for lying." This article showcases some of the common applications and issues of today's commercially available lithium-ion batteries.



A specific power vs. specific energy plot demonstrates the superiority of lithium-ion battery technology over traditional aqueous batteries and supercapacitors. The "C curves" on the right side of the plot represent the discharge times — C/10 is a ten-hour discharge (a slow rate for low-power applications), C (or C/1) is a one-hour discharge, and 100C (or C/0.01) is a 0.01-hour discharge (a very fast rate for high-power applications). For instance, a medium-power Li-ion cell that weighs 1 kg in a device that draws 120 W will provide 130 Wh of energy and be fully discharged in 1 hour. The same cell under a 15-W load will provide 150 Wh of energy and be fully discharged in 10 hours. Graph courtesy of Saft.

Tailored to the application

Several choices are available for the cathode and anode in a Li-ion battery, and they are selected based on the desired performance.

Cathode selection. Spinels (*e.g.,* $LiMn_2O_4$) and olivines (*e.g.,* $LiFePO_4$) have flat voltage profiles and experience relatively small volume changes during delithiation, but typically have lower energy densities. These cathodes are preferred for applications demanding high power and are generally considered the safest of cathode choices. $LiCoO_2$ (LCO) is a common cathode used in portable electronics, as it provides a good balance between energy density and stability, but its use is often limited by the cost of cobalt. Nickel can be added to the layered LCO structure to reduce the cobalt content and enhance the energy density — these cathodes fall into two general classes: NCA (*e.g.,* $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) and NMC (*e.g.,* $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$).

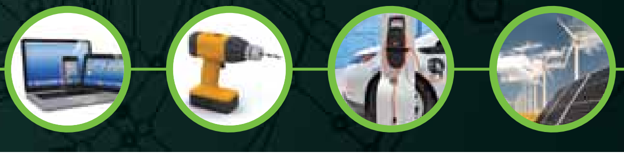
There are no rules to follow in choosing a cathode material for a specific application. As with everything else, it comes down to cost and the physical limitations (volume, weight, temperature, etc.) of the application. Money saved on lower-cost cathodes may be spent on higher-cost battery management systems (BMS) and enhanced safety designs. Since lithium-ion batteries are typically incorporated into a larger electrical product, and rarely sold directly to the consumer, the final product designer must weigh the tradeoffs of the cell's chemistry.

▲ **Figure 1.** Lithium-ion cells with rigid containers may have a cylindrical or prismatic design. These cells are often combined in series to make battery modules (and modules are combined in series and parallel configurations to make battery packs). Photo courtesy of Johnson Controls.

Anode selection. Graphite is the predominant anode material for lithium-ion systems, because it has relatively high capacity (compared to cathode materials) and operates within 100 mV of lithium metal. Hard carbon is also used, but it generally has a lower capacity than graphite and operates a few hundred mV above lithium, which lowers the energy density of the cell. Due to hard carbon's sloping voltage profile, it is often paired with cathodes that have flat voltage profiles, such as spinels and olivines. A sloping voltage profile provides a convenient state-of-charge (SOC) indicator.

Silicon anodes have attracted attention due to their theoretical capacity of 4,200 mAh/g for fully lithiated silicon, which is more than ten times that of graphite's 360 mAh/g. However, silicon particles swell 400% when fully lithiated, which causes particle fracturing that drastically shortens anode life. For this reason, silicon is usually blended with graphite and the degree of lithiation is limited.

The closer an electrode operates to the potential where lithium metal forms deposits, the more reactive the material becomes. The anode considered the safest is lithium titanate spinel ($Li_4Ti_5O_{12}$, or LTO), which has an open circuit



potential of 1.55 V vs. lithium. Unlike other anode systems, LTO does not expand or contract during cycling. However, the reduced energy density of LTO-based cells limits their use to applications demanding the highest level of safety and/or long life. Another benefit of LTO-based cells is their high power capability — due in part to their spinel structure, which allows lithium ions to diffuse into the crystal structure in all three dimensions.

Electrode selection. When choosing electrodes, the first step is to determine the thickness of the electrodes. High-power applications generally favor thinner electrodes (~30 µm), while high-energy applications favor thicker electrodes (~50–100 µm). There are tradeoffs to both types of electrode. Thin electrodes require more electrode surface area, which in turn requires more copper and aluminum current-collecting foils and more separator. Electrodes that are too thick can cause non-uniform current distributions throughout the thickness of the electrode, which underutilizes the material closest to the current-collecting foil while overstressing the material closest to the separator.

Packaging selection. Packaging may be either rigid or flexible (*i.e.,* a can versus a pouch). Rigid containers are usually made of steel or aluminum and offer the most protection for the cell contents. They are also able to contain higher internal pressures (up to 200 psi) before venting through a rupture disc. Flexible packaging offers the convenience of easier cell assembly by simple hot-sealing methods, but it provides less protection for the cell contents and generally cannot contain internal pressure of more than 30 psi.

Some packaging represents a hybrid approach, such as several pouch cells combined in a sealed metal container. Another hybrid approach uses a pouch laminate with a much thicker aluminum barrier layer sandwiched in the middle, but thin enough that the pouch laminate is still heat-sealable — essentially a stiff pouch.

Design selection. Cell designs may be either cylindrical or prismatic (Figure 1). The most common cylindrical cell used in portable applications such as laptops and power tools is the 18650 format, which is 18 mm in diameter and 65 mm high. Prismatic designs are used where flat profiles are needed, such as in cell phones. Thermal-management criteria impose limits on the thickness of each design, with the diameter of cylindrical cells generally less than 6 cm and the thickness of prismatic cells generally less than 4 cm.

Applications for Li-ion batteries

Lithium-ion batteries were commercialized by Sony in 1991 for audio-video equipment, laptop computers, cellphones, and other portable equipment. They have become the battery of choice for nearly every portable device on the market due to their higher voltage, higher energy density, lack of memory effect, and relatively long life.

The high voltage provided by lithium-ion batteries means that fewer cells in series are needed to achieve a desired voltage. For instance, a graphite/$LiMO_2$ battery has an average voltage of 3.6 V and can replace three NiCd or NiMH batteries, which have an average voltage of 1.2 V. This feature alone has saved considerable space in portable electronics by enabling reductions in hardware size and void space.

Lithium-ion batteries are also designed to be fabricated in a variety of electrode and cell configurations to fit a wide range of power and energy applications. Cost aside, in most applications, lithium-ion batteries have superior power and energy density over conventional aqueous rechargeable batteries.

Portable electronics

The majority of lithium-ion batteries for portable applications are made in Japan, South Korea, and China, which reflects the fact that the majority of portable electronic devices are made in Asia. SignumBOX (based in Chile, the location of the largest lithium salt brines) publishes an annual analysis of the lithium market that reports the end uses of lithium by application *(1)*. In 2012, it estimated that 33% of lithium production was used in rechargeable lithium-ion batteries, while only 2% was used in primary lithium-metal batteries (most of the remaining lithium was used for frits, glass, grease, etc.). Table 1 provides a further

Table 1. Estimated consumption in 2012 of lithium in Li-ion batteries for various uses.

Application	Amount of Lithium Consumed, m.t.	Number of Units, millions	Typical Unit Size	Typical Li Content, g/unit
Laptops	2,050	585	2.0–3.0 Ah (40–60 Wh)	2.8–3.8
Mobile Phones	360	1,700	1.0–1.2 Ah	0.14–0.19
Smartphones	130	530	1.5–1.8 Ah	0.21–0.27
Tablets	230	120	20–30 Wh	1.4–1.9
Power Tools	140	–	50–60 Wh	3.3–3.8
Other Electronics	460	–	–	–
Electrified Vehicles	500	0.4	0.5–60 kWh	30–3,800
Smart Grid	94	–	0.01–5 MWh	630–310,000
Total	**3,964**			

Notes: Values have been converted from weight of Li_2CO_3 to weight of lithium metal. The sizes of electrified vehicles and Smart Grid batteries were estimated by the author. Laptop batteries are usually sold in series of six cells. Source: Adapted from Ref. 1.

breakdown of the end-use estimates for lithium-ion batteries in 2012. Laptop manufacturing consumes the largest amount of lithium, while mobile phones and smartphones consume the most lithium-ion batteries. China reportedly made more than 4.5 billion lithium-ion batteries in 2011 alone.

Moore's Law is the observation that the number of transistors on integrated circuits doubles approximately every 18 months to two years. The result of this miniaturization bonanza has enabled the computing power that once required a large room to now fit nicely in a pocket. These technological wonders demand ever more energy, and today the largest component in any portable computing device is the lithium-ion battery.

Moore's Law does not apply to batteries due to the nature of the charge carrier. Electronics utilize electrons, whereas batteries utilize ions, and the volume of a lithium ion is 10^{13} times larger than that of an electron. The semiconductor industry has now miniaturized the electron's conductive path to a width of mere atoms (which implies that Moore's Law may soon no longer apply to electronic circuits). However, ions flow through bulky electrolyte channels that are already essentially at their minimum width.

Incremental improvements in the energy density of lithium-ion batteries will continue, but it is unlikely that an order of magnitude increase will ever be possible. Even a doubling of the energy density is highly ambitious. Hence, researchers are now discussing what the next battery technology beyond lithium-ion may be.

▲ **Figure 2.** The Chevy Volt was the first large-production PHEV using a lithium-ion battery (made by LG Chem). The battery pack provides 16.5 kWh of energy, weighs 435 lb, has a nominal system voltage of 355 V, and is comprised of 288 cells with a nominal capacity of 15 Ah each. Photos courtesy of General Motors.

Transportation

Thomas Edison did not lose complete faith in batteries. A decade after he made his critical comments, he began a nearly 20-year effort to develop and improve the nickel-iron battery to power an electric car. In 1899, an electric car running on lead-acid batteries achieved a record speed of 65.79 mph *(2)*. Gas-powered cars were in their infancy at the start of the 1900s and were outnumbered by electric cars.

That all changed in 1909 when Henry Ford rolled out the affordable mass-produced Model T, which took advantage of the abundance of a newly discovered fossil fuel called petrol (gasoline). The rapid-refueling capability of gasoline-powered vehicles, coupled with the advent of the electric starter, soon put electric vehicles out of favor. Batteries, ironically, powered the electric starter.

It wasn't until the oil crises of the 1970s and 1980s that the electric vehicle market experienced a resurgence, which was further boosted in the following decades by the worries of greenhouse gas emissions and peak oil.

Several types of electrified vehicles (EVs) have been commercialized: hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and battery electric vehicles (BEVs).

HEVs typically have a 0.3- to 1-kWh battery that provides power assist and regenerative braking to the vehicle while relying on an internal combustion engine to provide the range. It does not need to be plugged in; instead, it is charged by a generator connected to the drive train.

PHEVs typically have a 3- to 16-kWh battery that provides an electric-only range of 10–40 miles (in a charge-depleting mode) before a gas engine engages to extend the range. The PHEV then enters a charge-sustaining mode and operates as an HEV, and the battery is later charged at the user's convenience.

The BEV is perhaps the simplest of vehicles in terms of components. It does not have an engine, but instead relies only on the battery for range and must be recharged when depleted. Range anxiety is the main concern about BEVs — a 30- to 60-kWh battery will take a BEV sedan 200 to 300 miles, depending on vehicle weight and climate. HEVs and PHEVs, on the other hand, do not induce range anxiety — they operate as fuel-efficient vehicles even if the battery is depleted.

HEVs have enjoyed the most consumer acceptance of all electrified vehicles. The most popular HEV, the Toyota Prius, was first released in Japan in 1997 and in the U.S. in 2000. Toyota has now sold over 5.3 million hybrids worldwide, with over 2 million of those sold in the U.S *(3)*. While the majority of its hybrids are based on nickel metal hydride batteries, Toyota has been implementing lithium-ion batteries in their new plug-in version of the Prius (as well as the RAV4-EV and the European Prius+). Last year, Toyota

announced plans to create a new lithium-ion battery production line with Panasonic that will have the capacity to make 200,000 batteries a year *(4)*.

In a leap-frogging move, General Motors led an aggressive effort to develop the technologically advanced Chevy Volt (Figure 2). The first commercially available PHEV, the Volt is based on a 16.5-kWh lithium-ion battery manufactured by LG Chem that provides a 38-mile range under most driving conditions. The release of the Volt in December 2010 prompted Toyota to include a limited PHEV range for one of the Prius models starting in 2012, and set the bar high for the rest of the fuel-conscious auto industry. Over 46,000 Chevy Volts have been sold, with monthly sales this year averaging near 1,800 *(5)*. Ford also released two PHEVs in 2012 — the Ford Fusion Energi and the Ford C-Max Energi — which have a 7.6-kWh lithium-ion battery for a 21-mile EV range.

BEVs currently on the market include the Ford Focus Electric, Mitsubishi i-MiEV, Tesla Model S (and Roadster), and Nissan LEAF. All of these BEVs have lithium-ion batteries due to their high energy density. Nissan has sold over 33,000 LEAFs in the U.S. since its release in December 2010, with monthly sales averaging over 1,700 in 2013. The LEAF uses a 24-kWh lithium-ion battery to power an 80-kW motor for a nominal range of 75 miles. The sportier Tesla Model S has reached production levels of 400 per week, with sales of more than 13,000 in the U.S. in 2013. The Model S, with a rated range of 300 miles, uses a 60-kWh battery based on the widely available lithium-ion 18650-format cells that were originally developed for portable applications (*e.g.,* laptop computers and power tools). U.S. sales of the Ford Focus Electric and the Mitsubishi i-MiEV have approached 1,900 and 600, respectively, since January 2012.

Sales of electrified vehicles are projected to increase worldwide over the coming decade, with BEV sales reaching one million by 2020 (Figure 3).

Battery cost is the major limitation of BEVs, and to a lesser extent PHEVs. Current lithium-ion batteries cost around $600/kWh. This price needs to be closer to $300/kWh before consumer acceptance of PHEVs and BEVs increases significantly.

Passenger cars are not the only vehicles being electrified. The U.S. Dept. of Energy (DOE) recently announced an electrification initiative through which it ordered 120 large plug-in hybrid work trucks powered by lithium-ion batteries.

Electric bikes (e-bikes) are also benefitting from the high energy density of lithium-ion batteries. As the price of lithium-ion batteries continues to fall, more e-bikes are being offered with lithium-ion batteries. Global sales of e-bikes are now nearly 30 million annually (mostly in China) and are expected to increase to 40 million by 2015 *(6)*.

Earlier this year, Johnson Controls, the world's leading automotive battery manufacturer, announced that it will make the lithium-ion battery pack for Torqeedo's all electric, 80-hp Deep Blue boat *(7)*.

Grid energy storage

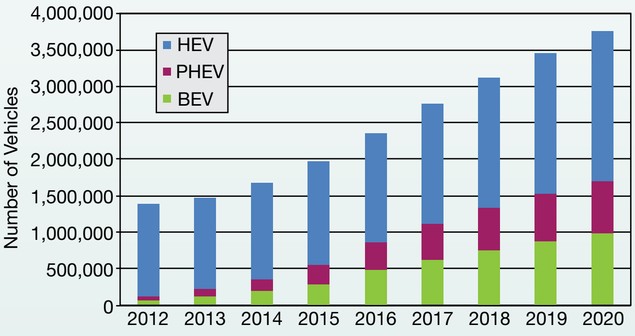
Large windmill farms are becoming a common sight in rural areas with dependable wind patterns. More wind (and solar) farms can be expected as the world incorporates renewable energy sources into the energy mix. One major drawback for wind and solar is their inherent intermittent power production. Utilities consider only 10% of the total installed capacity coming from most renewable energy sources as being readily available. This is commonly referred to as dispatchable capacity in the utility industry. Hence, up to 90% of solar and wind rated capacity must be backed up by other generating resources, such as natural gas, coal, nuclear, or energy storage.

Adding energy storage systems to the grid enhances its performance and reliability regardless of whether it receives any input from renewable energy sources. Grid energy storage falls into three general overlapping categories:

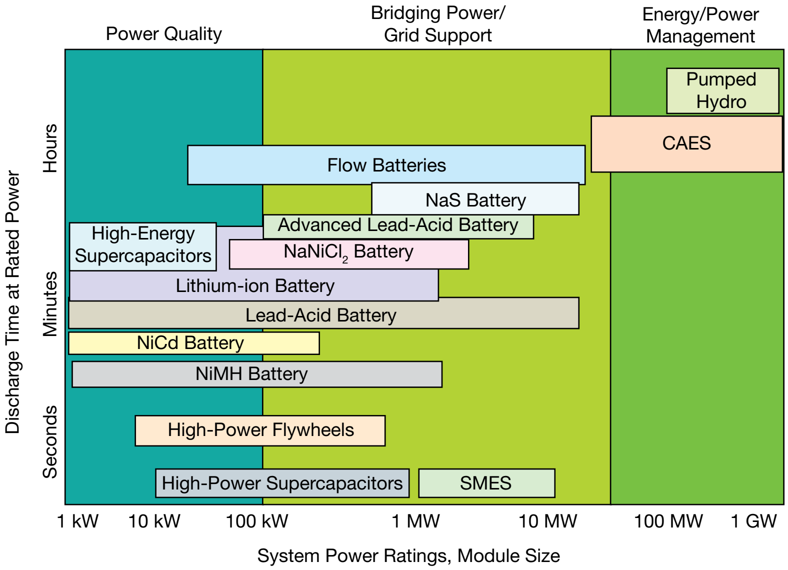
- power quality systems, which inject short (less than one second) bursts of power into the grid for frequency regulation
- bridging power/grid support systems, which inject power over several seconds to minutes during switching of energy sources and some load shifting
- energy/power management systems, which provide hours of energy to allow load leveling (or load shifting, which is the transfer of lower-cost energy to higher-priced demand).

Typical energy sources that cover these grid applications are shown in Figure 4, which is a pseudo log-log plot of discharge time versus system power rating; a higher discharge time corresponds to more energy provided at a desired power level.

Lithium-ion batteries are suitable for high-power appli-



▲ **Figure 3.** Sales of electrified vehicles are projected to increase worldwide, with BEVs reaching one million vehicles by 2020. Source: Navigant Research.



▲ **Figure 4.** Energy storage for use on the electric grid could employ a variety of technologies. Lithium-ion batteries are well suited for stationary storage systems that supply several minutes to an hour of energy, at power levels up to a few MW. Source: Sandia National Laboratories.

cations in grid energy storage for frequency regulation, but due to their high cost they are not as widely used in load leveling/shifting applications. However, this is beginning to change. Earlier this year, EnerDel commissioned a 5-MW smart grid system for Portland General Electric (PGE) consisting of 1,440 lithium-ion battery modules that should be able to power 500 homes *(8)*. A123 Systems (with partner AES Energy Storage) has installed over 100 MW in energy storage projects *(9),* including one on the island of Maui that can deliver 11 MW for short durations. A123 Systems recently installed a longer-duration system capable of supplying 1 MW of power for 1 h (1 MWh of energy) on the same island. That system, which fits in a 20-ft cargo container, is based on lithium-ion nanophosphate prismatic cell technology. For even more power, A123 Systems' single 53-ft Grid Battery System can supply 4 MW for one hour *(10)*.

Southern California Edison (SCE) selected LG Chem to install a 32-MWh battery energy storage system (BESS) for the Tehachapi Wind Energy Storage Project *(11)*. This will be the largest BESS in North America, residing in a 6,300-ft^2 facility, and will have the energy equivalent of 2,000 Chevy Volt batteries. Saft offers the Intensium Max 20E lithium-ion BESS, which can store 1 MWh and discharge at a 500-kW rate and is housed in a standard 20-ft cargo container *(12)*. Altairnano's Alti-Ess Advantage, a 2.0-MW system based on a nanostructured lithium-titanate (LTO) battery, is designed for fast-response applications that demand high power, such as grid stability, renewables integration, and frequency regulation *(13)*.

Factors that impact Li-ion battery performance

Temperature can have the biggest impact on lithium-ion battery performance (Figure 5). The typical operating temperature window for Li-ion technology is –20°C to 60°C for charging and –50°C to 60°C for discharging. Lithium-ion batteries experience significant power loss below 0°C, as evidenced by the lower operating voltage in Figure 5. Charging at a current rate that is too fast, especially at low temperature, may cause lithium dendrites to form on graphite anodes, since the graphite cannot accept the lithium ions fast enough. Lithium dendrites reduce the cycle life of the cell and may cause overheating, which causes deleterious side reactions within the cell that will also shorten the life and may create safety issues.

Properly designed cell/battery systems can usually provide over a thousand discharge cycles at 80% depth of discharge (DOD), while tens of thousands of cycles can easily be achieved with shallow discharges. Calendar life and cycle life are not the same thing: Calendar life is the expected total length of time that the battery is usable, similar to shelf life or storage life, whereas cycle life is the expected number of times a battery is charged and discharged. Both can be extended by limiting the amount of time that a cell is stored at top of charge, where the chemistry is most reactive.

Safety hurdles

While the nonaqueous electrolytes in lithium-ion batteries have enabled the use of cell couples that operate across a 4.5-V potential window, most of these electrolytes contain a flammable organic carbonate solvent. Nonflammable electrolytes (including polymer-based electrolytes) are available, but they tend to suffer from a narrower potential window and/or lower ionic conductivity.

Under normal operating and storage conditions, a flammable electrolyte is not a safety hazard. Hazards exist when the battery is outside of its safe operating zone or if a defect in manufacturing becomes apparent sometime during its life.

Several features are incorporated into properly designed cells to ensure safety, such as circuit breakers or fuses, and rupture discs. In addition, a thermal-management system maintains the temperature of the cell/battery within an acceptable range. Thermal-management systems can be either active or passive, and use air or liquid as the heat-transfer medium. AllCell Technologies has developed a passive thermal-management system based on phase-change materials to control the battery temperature.

Lithium-ion batteries can be especially hazardous if they

are overcharged or overheated. Overcharging lithium-ion cells with graphitic anodes by even just a few hundredths of a volt can cause the formation of lithium metal dendrites, which then generate internal heat as the fresh high-surface-area metallic lithium reacts with the electrolyte to form a passivation layer. A snowball effect may occur if the heat is not drawn away from the cell fast enough, because the increased temperature will cause additional side reactions to occur.

If the cell temperature reaches 70°C to 90°C, the cell may self-heat to the point of thermal runaway. Thermal runaway is the rapid release of a cell's stored energy, and is the biggest concern of battery developers. Thermal runaway is not limited to cells with graphite anodes; all cells can experience it under certain conditions. There is ample footage posted online of laptops and cell phones undergoing thermal runaway. These images are jarring and reinforce the need to design battery applications with caution.

Battery management systems (BMS) are typically deployed to monitor and improve Li-ion battery performance and ensure safe operating conditions. A basic BMS monitors the voltage and temperature of the battery. More-complex systems also monitor the voltage and temperature of each cell. Even-more-complex systems adjust the voltage of individual cells in series configurations (*i.e.,* cell equalization) to prevent a cell from being incrementally overcharged with repeated cycling.

Quality control is extremely important in lithium-ion battery production, not just for performance and life, but also — especially — for safety. The negative and positive electrodes are usually separated by only 20 µm, and often this separator is a porous sheet of a polyolefin that melts at 110°C to 135°C. An internal short can develop if a small conductive particle lands on the separator during assembly. For this reason, many assembly rooms actively filter the air to remove particles larger than 5 µm. Internal shorts are troublesome because there is no reliable way to detect them once the battery is in the consumer's hands.

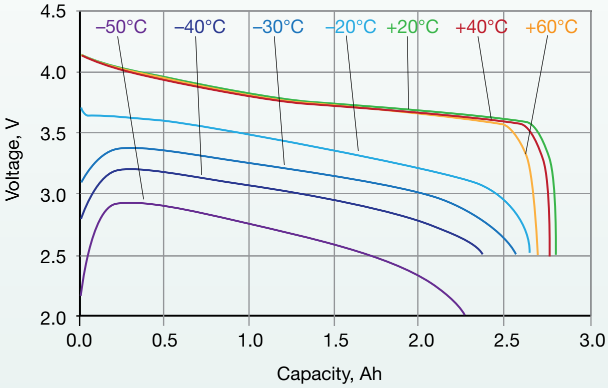
After a lithium-ion battery is sealed, it undergoes a formation/break-in process during which the cell is carefully charged and discharged to form a robust passivation layer referred to as a solid electrolyte interface (SEI) layer. After formation, the cell is monitored for several weeks in an effort to detect defective cells. Cells with hidden contamination particles that have high aspect ratios can pass this quality control step if they are oriented parallel to the electrode/separator interface, and they may never cause a concern if they remain in that orientation. However, electrodes expand and contract by small amounts during cycling. These movements may cause the particle to orient itself perpendicular to the electrodes and create an internal short. Any current-limitation device or internal fuse is useless once an internal short forms, because all of the cell's energy passes through the short. This creates a rapid temperature rise that may trigger a thermal runaway. If the cell is in a battery configuration, all of the battery's energy will pass through the short, too, if the battery design does not have proper fusing.

Beyond Li-ion

While developers continue to make incremental improvements in the energy density, performance, and cost of lithium-ion batteries, the question being asked now is "what's next?" Electronic devices are demanding more energy with each new generation, as consumers expect more features. In addition, the corporate average fuel economy (CAFE) standard of 54.5 mpg by 2025 will require increased electrification of the vehicle fleet. Growth in the deployment and use of renewable energy sources will require increases in large-scale energy storage for power grids. Cleary, a quantum leap in battery technology is necessary.

DOE has responded to this challenge by establishing an energy innovation hub that involves a consortium of academia, national laboratories, and industry. The Joint Center for Energy Storage Research (JCESR), headquartered at Argonne National Laboratory, brings together many of the world's leading battery researchers around the common objective of improving energy systems by overcoming fundamental challenges.

JCESR aims to go beyond today's best Li-ion systems to provide five times the energy storage at one-fifth the cost within five years. Meeting this ambitious goal will require the discovery of new energy storage chemistries through an atomic-level understanding of energy storage phenomena and the development of universal design rules for battery



▲ **Figure 5.** The voltage of a lithium-ion cell varies as a function of temperature. This voltage profile is for a cell couple with a lithium cobalt oxide-based cathode with a graphite anode at a C/5 (5-hour) discharge rate. Note the sloping voltage curve as the cell is discharged, which provides a convenient method of determining state of charge. Lithium-ion systems experience significant power loss below 0°C because of high resistance. The unusual voltage rise early in the discharge phase at low temperatures is due to self-heating of the battery. Source: Saft.

performance. JCESR will focus on three electricity storage concepts that are broader and more inclusive than the technologies now being pursued by the battery community. These concepts include:

- *Multivalent intercalation.* This research focuses on ions such as magnesium, aluminum, and calcium, which carry two to three times the charge of lithium and have the potential to store two or three times as much energy.
- *Chemical transformation.* This work explores and exploits the chemical reaction of the working ion to store many times the energy of today's lithium-ion batteries, and will include the development of lithium metal and alloys that can be paired with oxygen or sulfur to create new storage technologies.
- *Nonaqueous redox flow.* This concept is based on reversibly changing the charge state of ions held in solution in large storage tanks; the very high capacity of this approach is well suited to the needs of grid energy storage systems. Some of the topics being explored in this field include: pumping slurries of electroactive solid materials as small particles; pumping solutions of dissolved organic species that are redox active; and/or combinations of these approaches with metallic anodes. CEP

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