Rechargeable Battery Science: A Survey of Advancements in Materials and Technology

ACS
Chemistry for Life®

Rechargeable Battery Science: A Survey of Advancements in Materials and Technology

About This Report

About The Author

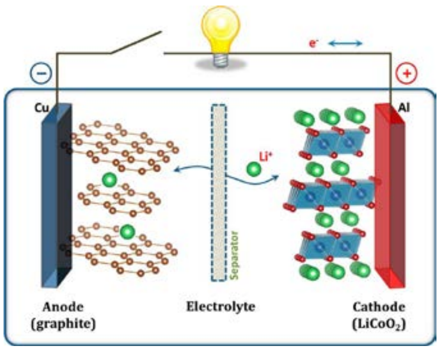
Prachi Patel is a freelance journalist based in Pittsburgh, PA. She writes about energy, biotechnology, materials science, and nanotechnology for various outlets including *Chemical & Engineering News*, *IEEE Spectrum*, *MRS Bulletin*, and *Scientific American*. She holds a master's degree in science, health and environmental reporting from New York University, and a master's degree in electrical engineering from Princeton University. She can be reached at prachi@lekh.org.

Cover images: Shutterstock

I. INTRODUCTION

Modern life runs on batteries. These energy-storing devices power things without which our lives would be unrecognizable: the phones in our palms, portable computers on our laps, and a growing number of hybrid and plug-in electric cars on the road. Batteries have come a long way since they first came to life at the turn of the 19th century. They have gone from large, leaky, unreliable contraptions to sleek, powerful packs that can take a vast range of shapes and sizes for different uses. Alkaline batteries, such as the familiar disposable AA type, can only be used once. They are an indispensible part of most households. But over 80% of today's battery market is composed of rechargeable batteries, also called secondary batteries. They are key to powering many of our everyday technologies, silently chugging along behind the scenes.

This report covers common rechargeable battery technologies — lead acid, nickel-based batteries, and lithium-ion — with a special focus on lithium-ion. Lithium-ion batteries have "enabled the wireless revolution of cell phones, laptop computers, digital cameras, and iPads that has transformed global communication," John B. Goodenough and Kyu-Sung Park write in a perspective article.[1] As these gadgets get more powerful and ubiquitous, there is a growing demand for batteries that can charge faster and last longer between charges.



Schematic illustration of the first Li-ion battery ($LiCoO_2$/Li^+ electrolyte/graphite).

Reprinted in part from: *J. Am. Chem. Soc.*, 2013, *135* (4), pp 1167–1176

DOI: 10.1021/ja3091438

Publication Date (Web): January 7, 2013

Copyright © 2013 American Chemical Society

Advanced batteries could be the foundation for a sustainable future. They will be key to moving away from fossil fuels for transportation and power generation. More affordable, powerful batteries will help to put more pollution-free electric vehicles on the road to replace gasoline-powered cars. And by storing electricity for entire cities to use even when there is no sun or wind, batteries could help unleash the full potential of renewable energy sources.

Batteries could also have a huge impact on economic growth in developing nations.[2] The use of generators for backup power is common in countries with unstable power grids. Batteries could supply power when generators fail, and could have an annual economic impact of $25 billion to $100 billion by 2025.

Coupled with solar chargers, batteries could uplift millions from poverty. About two-thirds of rural households in developing countries do not have reliable access to grid electricity. Providing electricity through batteries in remote areas could generate a value of $2–50 billion annually by 2025.

Requirements for batteries are exhaustive and depend on their purpose. Batteries for consumer electronics have to be small, pack a lot of energy, and be affordable. Electric car batteries need to be safe, reasonably priced, charge quickly, carry a lot of energy to take the vehicle long distances, be able to release that energy quickly for acceleration, and last a long time. Most of today's battery research focuses on lithium-based systems. Lithium-ion is a dynamic, commonly used technology because it packs a lot of energy in a small volume. Lithium-ion dominates the growing portable electronics and electric vehicle markets.

Yet for all the advances over the past decades, lithium-ion technology still faces many challenges. The batteries are still costly, take a long time to charge, and can have a short lifespan. Many contain toxic elements, and can catch fire and explode. So far, no EV (electric vehicle) can go as far on a charge as a gasoline engine because gasoline contains 50 times the energy per weight of lithium-ion. The hunt is on for safer, cheaper, more powerful, and longer-lasting batteries, and promising breakthroughs are on the horizon. Some researchers are trying to double the capacity and halve the cost of lithium-ion batteries. Others are trying to make huge megawatt-scale battery systems that can power thousands of homes. Beyond lithium, there are many next-generation technologies brewing in laboratories around the world.

Making batteries more sustainable will be key as we use more and more of them. The same innovations that are making lithium-ion batteries a go-to also make these batteries harder to recycle. The surging lithium-ion battery market brings with it the risk of shortages in lithium, cobalt and other materials. Efforts are underway to develop greener chemistries; prolong the life of used batteries; and invent effective recycling technologies to keep batteries out of landfills.

II. RECHARGEABLE BATTERY BASICS

A Brief History

A battery is a device that stores chemical energy and produces electricity via a chemical reaction. It consists of a positive electrode (cathode), negative electrode (anode) and an electrolyte. During discharge, an oxidation reaction on the anode generates electrons that flow out of the battery through an external circuit to the cathode, producing electric current. Ions move between the electrodes inside the battery through a separator that keeps out electrons. Credit for inventing the first battery goes to the Italian scientist Alessandro Volta. The Volta cell, which he invented in 1800, was a stack of copper and zinc discs separated by a piece of cardboard soaked in salt water. Other battery chemistries and designs followed. But none of them could be recharged; they only produced an electric current until their chemical reactants ran out. That changed in 1859, when French physician Gaston Plante invented the first rechargeable battery based on lead and acid, the same system still used today. Other rechargeable batteries evolved over the decades: nickel-cadmium in 1899, nickel-metal-hydride in the mid-1980s, and then lithium-ion in 1977.

In a rechargeable battery, chemical reactions that occur during discharge can be reversed by passing an electric current through the device in the opposite direction. This restores the battery's charged state and allows it to be used over and over again. Recharging can take minutes to hours. The invention of the rechargeable battery was a gamechanger. It was a key breakthrough that sparked the electrification of Europe and America in the late 19th century.[3] It also enabled some of the very first electric cars. In the early 1900s, electric cars were a common sight on city streets because they were quiet, emission-free, and easier to drive than hand-cranked gasoline cars.

Important Traits

To assess a battery's performance for a particular application, it is important to look at both electrical characteristics and physical traits like overall size and weight.[4] A critical figure of merit for a battery is the energy density, the amount of energy, measured in Watt-hours, that it can hold in a given weight or size. Battery energy density is measured in Wh/kg or Wh/l. It impacts the battery's runtime, or how long it can go between charges. That in turn determines an EV's driving range or how long a phone lasts before needing to be plugged in. A battery's lifespan — which is different from runtime — signifies how many times it can be recharged. It is expressed in the number of charge cycles it can go through. After several charge cycles, batteries start losing their capacity after enough chemicals are built up and materials lost during reactions. In general, rechargeable batteries can last through 500 to 800 charge cycles.

A battery's cost is perhaps the most important criteria for consumers. Of commercial batteries, lead-acid is the cheapest, while lithium-ion is the most expensive. Researchers are trying to reduce the cost of lithium-ion by developing better, cheaper electrode and electrolyte materials. Cheaper packaging and longer lifetime will also help reduce overall cost.

Demand

Lead-acid systems have the largest share of the rechargeable battery market at around 61%, according to Grandview Research. In 2015, the global market for lead acid batteries was worth $33 billion, making it the most common battery in use, followed by lithium-ion at $16 billion.[5,6] Demand for lead-acid batteries is growing even as lithium-ion batteries are making inroads into some of the same uses. This is mainly due to booming construction and telecom industries and demand for personal vehicles in China, India and other Asia-Pacific countries. The global market for lead-acid batteries is expected to increase from around $53 billion in 2016 to over $81 billion by 2022.

While lead-acid batteries garner a bigger share of the market, lithium-ion batteries are a faster-growing market.[7] Electric vehicles and grid storage are going to drive battery demand in coming years. The concern now is whether manufacturers can keep producing batteries fast enough to keep up with demand.

Electric vehicles accounted for half of lithium-ion demand in 2016, and that demand will keep increasing. Battery-powered vehicles account for less than 2% of car sales today with around 1 million sold worldwide, but BNEF analysts expect sales to go up tenfold to 11 million by 2025.[8] By 2040, a third of all automobiles could be battery-powered, with 41 million electric vehicles on the road. Carmaker Tesla intends to double the world's supply of lithium-ion batteries by 2020 at its gigantic battery plant near Reno, Nevada, dubbed the Gigafactory.

Nearly every major car company is developing hybrid or electric vehicles.[9] Volkswagen plans to produce electric versions of all its cars by 2030. China, France, and the UK are pushing to eliminate gasoline and diesel vehicles and have all cars on their roads be electric in the coming decades. California, New York and New Jersey plan to spend $1.38 billion on charging infrastructure with the goal of getting millions of electric vehicles on the road.[10]

Grid storage could help utilities provide reliable and affordable electricity. Batteries can quickly provide extra power during times of peak electricity demand, especially in developing nations. As investment in renewable energy increases, batteries will be critical for storing intermittent energy produced from wind and solar farms.

Giant banks of lead acid and lithium-ion batteries are already starting to be used for storing wind and solar energy. Some of the largest grid storage projects in the U.S. include a 40 MW nickel-cadmium battery bank in Fairbanks, Alaska; a 36 MW lead-acid battery fleet at a Duke Energy company wind farm in Notrees, Texas; and a 32 MW lithium-ion battery at the Laurel Mountain wind farm in West Virginia.[11]

The world's largest battery storage system is in South Korea represented by the 150 MW lithium-ion battery built by Hyundai Heavy Industries and Korea Zinc to power the city of Ulsan.[12] Before that, the largest grid-scale battery was Tesla's 100 MW lithium-ion installation in South Australia, which can power 30,000 homes for an hour.[13] Similar projects are slated to come online soon. Southern California Edison is now constructing a 100 MW lithium-ion battery system. California utility PG&E has asked regulators to approve four enormous battery systems totaling over 560 MW of capacity. In an effort to decrease grid carbon emissions, California passed a bill in 2013 requiring its power companies to buy 1.325 GW of energy storage by 2020. Battery installations in California have gone up from 41 MW in 2014 to almost 150 MW in 2016.[14]

As costs fall, even more batteries will be used on grids, by homeowners who have solar panels, and buildings who want backup during power outages. Not counting car batteries, global storage capacity is expected to rise from 7 gigawatt-hours now to 305 GWh in 2030.[15]

III. RECHARGEABLE BATTERY TECHNOLOGIES

Lead-Acid Batteries

"Why mess with a good thing?" is an adage that applies well to lead-acid batteries. The battery has remained virtually unchanged since it was invented over 150 years ago. It is the oldest rechargeable battery system, and the first to be used commercially. Lead-acid has a relatively low specific energy of 30–50 Wh/kg, which is a fifth of lithium-ion. But despite its bulkiness, it remains a steadfast technology to this day, beating all others in ruggedness and at a low cost of $100–200 per kWh.

Lead acid is the workhorse starter battery for cars, trucks and motorcycles because it can provide the high current surge necessary to crank motor vehicle engines. But the batteries are also used to provide emergency backup power for telecommunications and computer centers; store energy for the utility grid; and to drive wheelchairs, forklifts, golf carts, and electric scooters and bicycles.

Each lead acid battery cell contains a spongy pure lead anode and a lead dioxide cathode. They are immersed, with a separator in between, into a plastic case filled with an electrolyte made of sulfuric acid and water. The size of the electrode plates and the volume of the electrolyte decides the amount of charge a lead acid battery can store. During discharge, when the battery provides electricity to the starter or headlights, sulfate ions migrate to the anode and react with lead to form lead sulfate. Electrons generated in this process flow out to provide electric current.

At the cathode, lead oxide reacts with the electrolyte to form water and some lead sulfate. The process is then reversed during recharge. Newer lead-acid battery types have emerged in recent years that charge faster, are lighter and more reliable.[16] One is an absorbent glass mat battery, in which the electrolyte is suffused into a specially designed fiberglass mat. Another is a gel battery, which contains sulfuric acid mixed with a silica gel.

Lead acid batteries suffer from limited lifespans of around 200–300 charge cycles and a long charge time of many hours. The culprit is lead sulfate accumulation on the pure lead anode. Scientists have found that replacing some or all of the lead on the anode with carbon suppresses lead sulfate formation. A handful of startup companies are experimenting with variations on this chemistry:

- Axion Power replaces the entire negative electrode lead with carbon.[17] This yields a battery that recharges faster and lasts longer than regular lead-acid systems. Because of the carbon anode, the battery also weighs 30% less. The downside is a lower energy density of 15–25 Wh/kg.
- The Ultrabattery developed by Commonwealth Scientific and Industrial Research Organisation (CSIRO) of Australia has a composite carbon-lead anode. More recently, researchers have experimented with carbon nanomaterials such as carbon nanotubes and graphene added to the anode that could improve performance and the lifetime of lead acid batteries.[18,19]

A typical car battery contains about 21 pounds of lead, and about 85% of the lead produced worldwide goes into batteries. The toxicity of lead is well known, and can cause a number of health problems when inhaled or ingested. The good news is that lead can be melted and reused indefinitely. Lead acid battery recycling is one of the most successful recycling programs in the world, partly because it is profitable.[21] In Europe and the U.S., nearly 100% of lead-acid batteries get collected and recycled. Over 12 billion pounds of lead was recycled from batteries in the U.S. between 2012–2016, according to Battery Council International. More than 60% of the lead used to make new batteries comes from recycling in the U.S and Europe. Lead battery recycling involves separating plastic from the lead compounds, which are smelted at high temperatures. This releases lead in wastewater and smokestack emissions. Recycling plants have strict emissions standards: their smokestacks require scrubbers to limit the number of lead particles that escape into the air. Many recyclers are now employing new technologies to lower emissions below what the law requires.[22] One company, Aqua Metals in Alameda, California, has developed a new recycling process that uses a more energy-efficient electrochemical process instead of smelting.

Nickel-Based Batteries

In 1899, Swedish scientist Wildemar Junger made a battery by immersing nickel and cadmium electrodes into a potassium hydroxide solution.[23] The nickel cadmium (NiCd) battery was the first to use an alkaline electrolyte. Commercialized in Sweden in 1910, it reached the U.S. in 1946. The battery's chemistry has several advantages. Nickel cadmium is one of the toughest and most durable batteries, able to withstand extremely high temperatures and lasting for well over 1,000 charge cycles with very little loss in its energy-storing capacity. It also charges very quickly and isn't expensive. For about 50 years, NiCd powered portable devices such as two-way radios, power tools, medical devices, and handheld video cameras. But the use of toxic cadmium was the battery's downfall. Environmental regulations now restrict the sale of NiCd batteries for most applications, although its ruggedness and safety has kept it the battery of choice for aircraft and trains, where they provide emergency backup power.

Nickel-metal-hydride (NiMH) chemistry has mostly supplanted NiCd.[24] Research on the NiMH battery started in 1967, when researchers swapped the cadmium anode with various metal alloys that absorb hydrogen. The first battery became available for commercial applications in 1989. Capable of storing twice the energy as lead-acid for the same weight, NiMH became the choice battery for portable electronics in the 1990s, until overtaken by the lithium-ion battery. Toyota picked the NiMH battery for the Prius and now nearly all hybrid cars use this battery chemistry. General Motors also used this battery for later generations of its now-defunct electric car, the EV1, which was launched in 1996. The commonly available rechargeable AA and AAA batteries made by Energizer, Duracell and other companies are also nickel metal hydride. However, NiMH has a small share in the battery market at 3%, and it is declining.

Lithium-Ion

As mentioned in the introduction, lithium-ion batteries have fueled the electronics revolution, enabling ultra-powerful smartphones and tablet computers, and are now revolutionizing transportation by allowing practical electronic vehicles with longer driving ranges.[25] The EV market, while still young, has overtaken portable devices as the biggest source of lithium battery demand. Lithium-ion also has the lion's share in grid storage, representing at least 97% of all storage capacity deployed in 2016.[26] By 2025, lithium batteries will make up 70% of the rechargeable battery market, followed by lead acid at about 20%.

Lithium is an ideal metal for a battery.[27] It is the lightest metallic element and has high-energy outer electrons that can easily take part in chemical reactions. Lithium has yielded batteries that are smaller and lighter than lead-acid and nickel-based batteries while producing the same power and with a longer charge. Today's batteries boast a high energy density of around 250 Wh/kg. The U.S. Department of Energy has funded the Battery 500 Project with aims to double this to 500Wh/kg. Pure lithium has a capacity of 3800 Ah/kg,

Lithium-ion batteries can be recharged more times than other batteries at 500–1000 cycles. Plus, they contain less toxic materials. Their costs have plummeted over the years, down from $1000/kWh in 2009 to about $200/kWh today, and are forecast to halve further to around $100/kWh by 2025.[14] But today's price still adds up for large automotive battery packs, which make up a third of an electric car's price tag. The Tesla and the Chevrolet Bolt have the longest driving ranges among electric vehicles today, but they are expensive and still have a standard range of around 250 miles after which they need to be recharged for several hours.

Chemist M. Stanley Whittingham pioneered lithium-ion chemistry while at Texas oil-giant Exxon, which supported energy storage research in response to the 1970s oil crisis.[28] Early batteries were dangerous and easily caught fire. They mostly used pure lithium metal as the anode and vanadium oxide as cathode. But the lithium metal anode grows tiny crystalline whiskers called dendrites that can tear through the separator and reach the cathode, shorting the battery and leading to fires.

Major breakthroughs in the next two decades gave rise to the popular lithium-ion battery of today. In the late 1970s, John Goodenough at the University of Texas at Austin developed cathodes made of lithium cobalt oxides, which now power portable electronics. He went on to make lithium manganese oxide cathodes, which power most of today's electric cars, as well as lithium iron phosphate cathodes that are used in power tool batteries. Sony Corporation, meanwhile, replaced the pure lithium anode with carbon, and released the first commercial lithium-ion battery in 1991. Currently, researchers are looking for ways to improve the battery by storing more ions in the lithium-ion anode, and shuttle them between electrodes faster and in a safe way.

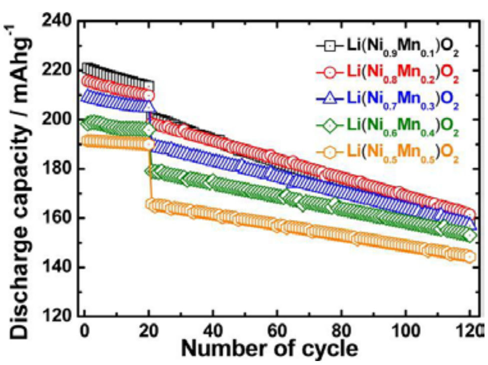
The Joint Centre for Energy Storage Research (JCESR), a consortium of researchers from U.S. national laboratories, universities and private companies launched in 2012 had an ambitious 5-5-5 plan to develop a battery that is "five times more powerful and five times cheaper in five years" with the help of funding from the U.S. Department of Energy. They have come close to meeting those goals, with a new battery that has three times the energy density and costs $120 per kilowatt-hour instead of the expected $100, and the DOE is now considering renewing the center's funding for another five years.[29] The UK government is pouring over $320 million into the "Faraday Challenge" launched in 2017 to boost battery research "aimed at overcoming battery challenges to accelerate the electric vehicle (EV) revolution."[30]

Cathode

Most advances in lithium-ion batteries in the past two decades have been related to the cathode.[31] A battery's cathode is a metal oxide and there are many different types, all containing lithium along with a mix of other metals. This choice of metals gives each battery different traits. Cathodes have a layered, crystalline structure to better store lithium ions. This structure can break down over time, causing batteries to lose their energy-storing capacity.

Batteries for portable electronics use lithium cobalt oxide in their cathodes. But the material is expensive and not very stable, which is why the capacity of electronics batteries starts to fade after a few hundred charge cycles. For electric cars, researchers have reduced cobalt and added nickel and manganese, which are more stable and affordable. Lithium nickel-manganese-cobalt (NMC) has become the most successful cathode material, and is used in power tools, e-bikes and electric cars. The Nissan Leaf battery has NMC cathodes, while the Tesla Model S does as well, adding aluminum to the mix. The NMC cathode usually has equal parts by weight of nickel, manganese and cobalt. Some car companies and battery manufacturers are pushing for much higher nickel content. Researchers at Argonne National Laboratory are working on cathodes that are rich in lithium and manganese.

There are also efforts to reduce or eliminate the use of cobalt in cathodes entirely. In May 2018, Tesla CEO Elon Musk announced that the company is slashing the use of cobalt in its battery cathodes and heading towards zero.[32] Another group is working on promising cobalt-free, nickel-rich cathode versions,[33] while Johnson Mathey is building a 1000 metric-tons-per-year facility to produce an enhanced lithium nickel oxide material.[34]



Discharge capacity vs cycle number of the Ni-rich $Li(Ni_{1-x}Mn_x)O_2$ ($0.1 \le x \le 0.5$) electrodes in a voltage window of 2.7–4.5 V at 55 °C. 1–20 cycles, 0.2 *C*; and 21–120 cycles, 0.5 *C*.

Reprinted in part from: *ACS Appl. Mater. Interfaces*, 2013, *5* (21), pp 11434–11440

DOI: 10.1021/am403684z

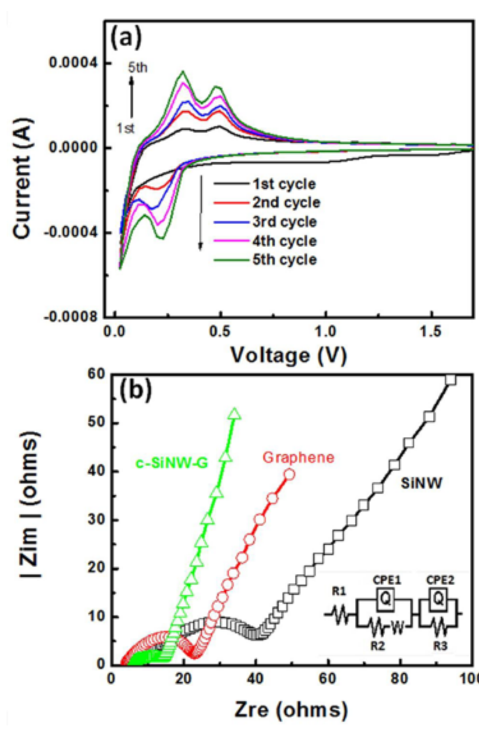
Publication Date (Web): October 15, 2013

Some experts advocate for making lithium-ion battery electrodes from common metals, such as iron and copper.[35] Lithium iron phosphate batteries are used commonly in power tools and remote-control hobby cars. Chinese electric buses already use batteries with lithium iron phosphate cathodes. Iron is an inherently safer cathode material than cobalt because the iron-phosphorus-oxygen bond is stronger than the cobalt-oxygen bond. So when the battery gets short-circuited or overheated, the oxygen atoms are harder to remove and don't cause a heat-generating chemical reaction. Compared to cobalt-based cathodes, they have a higher discharge current, do not explode under extreme conditions and weigh less. But they also have less energy density.

Anode

Advances at the anode are needed to usher in next-generation lithium-ion batteries with more storage capability. The anode in today's lithium-ion batteries is made of graphite, the same flaky carbon material used in pencils. But in the past decade, researchers have sought to return to metal-based anodes that were used in early lithium batteries.

Silicon has been studied extensively as a replacement. Produced from sand, silicon is cheap and readily available. It can also store ten times as much lithium by weight. The problem with silicon is that it swells to more than three times its size when it absorbs lithium ions, which breaks down the anode. Efforts to combat the swelling include using silicon nanostructures and combining silicon with carbon or the carbon nanomaterial graphene.[36,37,38] Tesla already uses some silicon in its batteries' graphite anodes, and BMW has also announced plans to use silicon-based anodes in its future electric vehicle batteries.[35] Other companies developing silicon-rich anode materials include Enevate, Enovix, and Sila Nanotechnologies, all located in California.



(a) Cyclic voltammogram for a coin cell fabricated using

(b) c-SiNW-G; (b) EIS for coin cells fabricated using c-SiNW-G, SiNWs, and graphene.

Reprinted in part from: *ACS Appl. Mater. Interfaces*, 2014, *6* (16), pp 13757–13764

DOI: 10.1021/am5032067 Publication Date (Web): July 31, 2014

A pure lithium metal anode would be ideal for batteries.[39] Lithium ions directly plate on the anode during charging and dissolve into the electrolyte during discharge. This allows the so-called lithium-metal battery to hold a large amount of energy per weight: 300 Wh/kg, one of the highest for lithium-based rechargeable batteries. But it also brings back the problem that Exxon and early battery pioneers in the 1970s faced: the growth of needle-like dendrites that can short the battery and cause fires. In 2010, a prototype lithium-metal battery with a capacity of 300Wh/kg made by German company DBM Energy was installed in an experimental EV that drove from Munich to Berlin on a single charge. Though not officially quantified, it is suspected that the car caught fire and was destroyed while on a laboratory test.

Armed with new materials and techniques, many researchers and startups are now pursuing lithium-metal as a next-generation battery. A hybrid lithium-silicon anode could be "the most promising anodes for advanced Li ion batteries that can realistically rival all kinds of carbon anodes," researchers at Bar-Ilan University say in a study.[40] Combining advanced cathodes with higher capacity anodes could increase the energy density of lithium-ion battery technology by 30%, they write.

Electrolyte

The conventional electrolyte in a lithium-ion battery is a lithium salt dissolved in an organic solvent. These solvents are volatile and can catch fire when overheated. Better electrolytes would make batteries safer and enable advanced high-capacity electrode materials that are on the horizon. There is a near-term need for liquid electrolytes that are compatible with graphite anodes and high-nickel cathodes.[25] At Pacific Northwest National Laboratory, researchers have made a fire-retardant electrolyte that does not catch fire even when exposed to a direct flame.[41] Researchers are also investigating various additives for electrolytes that would suppress lithium dendrite growth for safety. These additives include inorganic compounds like carbon dioxide, various organic compounds, or fluorinated compounds.[42] Other additives keep the battery from overcharging, and can even shut down the cell if it reaches a dangerous voltage. Ionic liquids, a group of nonflammable electrolytes, have also received research attention, but they are expensive.

Some teams are working on novel solidifying electrolytes that could protect batteries from getting crushed and catching fire.[43] The electrolytes are shear-thickening liquids like cornstarch dissolved in water, commonly known as "oobleck", which get thicker under pressure or impact. And there is a big research push for solid electrolytes, which would usher in a next-generation technology called solid-state lithium.
(See the section on Solid-State Lithium for more detail on this technology.)

V. LITHIUM-ION CHALLENGES AND CONCERNS

Safety

Any battery carries safety risks of electric shock, corrosive acids or flammable gases. But with hundreds of millions of lithium-ion batteries in use, failures, even though rare, have caught media and public attention. Several incidents over the past few years have highlighted the safety concerns associated with this type of battery. In 2013, the Boeing Dreamliner fleet of planes was grounded after batteries caught fire on planes. In 2016, reports of phones catching fire and even exploding led Samsung to recall its Galaxy Note 7 phones. Batteries in e-cigarettes and hoverboards have also sparked and flamed, causing injuries.

A lithium-ion battery can explode when its full charge is released instantly. A few different culprits can lead to this charge release. Microscopic metal particles floating in the electrolyte can gather in one spot, forming a bridge for high current to flow between the electrodes and overheat the battery. In efforts to make batteries lighter and thinner for electronics, the plastic separators between the electrodes have also become ultra-thin. If the separator breaks or gets punctured, the battery can short and catch fire. Batteries have also overheated and caught fire when overcharged, charged too quickly, or when left in heat or direct sun. Safety does remain a top concern in the battery industry. More stable electrode materials and non-flammable or solid electrolytes under development should help to make batteries safer. Some companies are also looking at complex coatings on the separators that can prevent the penetration of dendrites or conductive particles that can short the battery.

Material Supply

Can the supply of materials used in the lithium-ion battery keep up with booming demand? It's a question on the minds of many analysts, researchers, and car company executives. Of all the key materials that go into a battery, analysts have speculated most about looming shortages of lithium, cobalt, nickel, and graphite. A lithium-ion car battery with a 100 kg cathode uses 6–12 kg of cobalt and 36–48 kg of nickel.[35]

Of the materials listed, the supply of cobalt is the biggest concern. Most of the world's cobalt comes from mines in the Democratic Republic of Congo. The region is politically unstable and there are ethical concerns about the way the metal is mined in the country. Plus, it is difficult to extract. The combination of these factors add up to one thing: cobalt is expensive. In a recent study, researchers from MIT calculated that if 10 million electric vehicles were sold in 2025, the demand for cobalt could reach 330,000 tons while at most 290,000 tons of the metal would be available.[45]

Another study provides even starker numbers. If the projected 10–20 million electric cars are produced each year by 2025, electronic vehicles would need 100,000–200,000 tonnes of cobalt per year and 400,000–800,000 tonnes of nickel. Authors of the study expect that demand will outstrip production for cobalt by 2030 and for nickel by 2037 or sooner. Australia, Chile, Argentina, and Bolivia supply most of the world's lithium. Australia produces lithium by mining, while the South American countries produce it by evaporating the brine in salt lakes. A shortage of lithium is unlikely since resources are plentiful and the production from brine can be ramped up quickly to meet demand, the MIT researchers say.

Sustainability

While lithium-ion batteries could usher in clean energy and transportation, they also face an environmental challenge at the end of their lives. Electric car batteries are designed to last for about 8 years, but many start losing their capacity, and hence their driving range, after 5 years. At the end of that, they are removed from cars but still have as much as 80% of their capacity left. Faded electric vehicle batteries could be used to store wind and solar energy on the grid or as backup batteries at home. But they are most likely to end up in landfills. Only about 5% of electric vehicle batteries are recycled today because of a lack of incentives, policies, and recycling infrastructure. This is wasteful and harmful to the environment, and also uneconomical given potential material supply risks, as mentioned earlier. Additionally, the manufacturing of lithium-ion batteries takes a lot of electricity. Recycling could cut the environmental impact of batteries by reducing the amount of electricity and mined material needed for their production, and by keeping plastics and hazardous materials out of landfills.

Recycling Challenges

Nearly all lead-acid batteries get recycled.[44] Lead is heavily regulated due to its toxicity. Lead-acid batteries are standard-sized and are made up of only a few different components, so they are easier to break apart and recycle profitably. That's not the case for lithium-ion. Achieving a closed-loop economy for lithium-ion technology is not easy because of their different complex chemistries, components, and sizes. Much research has been done on recycling technologies. Some companies, such as Umicore and Retriev Technologies, already recycle on a large scale, but the processes either do not recover lithium or recover it with impurities.

Lithium-ion recycling efforts efforts focus on the cathode since that makes up a large percentage of battery mass and contains valuable metals. The conventional method involves melting the battery and recovering individual elements, which is profitable for high-value metals like cobalt. But as battery-makers are moving away from costly cobalt to more plentiful iron and manganese, the economical incentive to recycle cathodes goes down. For example, recovering battery-grade manganese and lithium from lithium iron phosphate and lithium manganese oxide batteries via recycling is more expensive than mining these materials.[45]

Several researchers and recycling companies are now trying to develop a method called direct recycling, which would recover the entire cathode compound, made from lithium nickel manganese cobalt oxide for example, for reuse in a new battery. The process involves shredding the battery electrodes, separating cathode materials using sieves or magnets, purifying them, and then adding the desired ratio of lithium, manganese, cobalt, and nickel. This method works for most lithium metal oxides.

At least three startups are now developing direct recycling technology: Battery Resources, a Worcester Polytechnic Institute spinoff; OnTo Technologies in Bend, Oregon; and battery maker Farasis Energy in San Francisco.

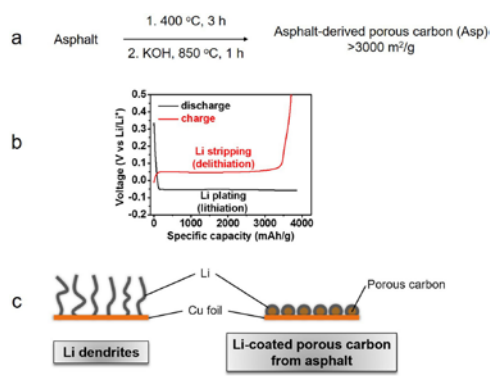
- Battery Resources' process can recycle up to 80% of the cathode materials from unsorted batteries and could cut the cost of cathode materials by a third.[44] A new pilot plant that became operational in the summer of 2018 can recycle 500 kilograms of batteries every day.
- Farasis' process involves discharging battery cells, removing the electrolyte, and then separating plastic and metal components using sieves or magnets. The electrodes are crushed to give a powdered mixture of anode and cathode materials, conductive carbon and binders, and trace metal particles. These materials are separated and purified. Then with the addition of some more lithium to the cathode material, it is ready for use in new batteries. Once the refurbished cathode material is ready, the company does surface chemistry to match its energy-storing capacity with that of virgin materials. In early 2017, Farasis received a two-year grant of $1.76 million from the United States Advanced Battery Consortium to take its process from the lab to a larger scale.
- Onto uses a similar method to Farasis', physically separating battery components and then pulverizing them to give a black powder of mixed anode and cathode materials.

The lithium-ion battery has improved steadily over the past 30 years and has displaced other battery technologies as a result. But the technology's energy density is reaching its fundamental limits and improvements are slowing down. Plus, there's a dire need to make electric vehicles and grid storage more affordable. "The race to build the next revolutionary battery is heating up," writes Akshat Rathi in a recent article in Quartz.[56] "Just in the first half of 2018, investors have pumped into battery startups double the amount they invested in all of 2017." Some of these potential successors promise to pack up to ten times more energy per kilogram than conventional lithium-ion. Others are gearing up for the post-lithium era and using more plentiful, cheaper materials.

Lithium-Metal

Lithium-metal battery technology swaps the graphite anode in conventional lithium-ion batteries with pure lithium metal, which helps the battery hold more energy. Canadian startup Moli Energy was the first to market lithium-metal batteries in 1989, but the devices started catching fire, leading to recalls. The company declared bankruptcy soon after. After undergoing restructuring and refocusing its research efforts, it was bought by Taiwanese lithium-ion battery manufacturer E-One in 2000.[46,47] E-One Moli Energy now sells more traditional lithium-ion battery cells with graphite anodes.

As discussed previously, metallic anodes suffer from dendrite growth that can short batteries. Researchers are now working on suppressing dendrites by using special coatings on the anode,[48] putting protective nanodiamond thin films on the anode,[49] or nanodiamonds to the electrolyte.[50] A team at Rice University made lithium metal anodes by coating lithium on a porous asphalt-graphene substrate;[51] the resulting battery showed a remarkable energy density of over 900 Wh/kg, was super-fast charging and had no dendrite formation.



(a) Preparation of porous carbon from untreated gilsonite. (b) Charge/discharge profile for preparation of Asp–GNR–Li anodes. (c) Schematic illustration of the typical lithium dendrites (left) vs the lithium-coated high surface area porous carbon from asphalt (right).

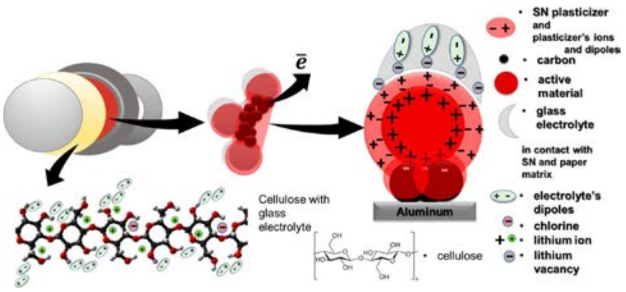
ACS Nano, 2017, *11* (11), pp 10761–10767
DOI: 10.1021/acsnano.7b05874
Publication Date (Web): September 27, 2017

Another group has found that applying heat can melt the dendrites and smooth the anode.[52] Pellion Technologies, a Massachusetts-based startup claims that they have built a reliable lithium-metal battery and have been selling it to a drone maker since February 2018.[53] While Pellion's batteries can hold twice the energy of conventional lithium-ion, it is not cheap, usually takes three hours to charge, and has a limited lifetime of 50 charge cycles.

Solid-State Lithium

Solid-state batteries are widely considered to be the next big breakthrough for battery technology. Solid-state batteries replace the volatile liquid electrolyte with one that is solid. In addition to being non-flammable, the solid electrolyte also blocks dendrites from forming, so it would allow the use of lithium metal electrodes. The resulting battery promises to be safer and to store twice the energy of conventional lithium-ion batteries.

The electrolytes used in solid-state batteries can be polymers, ceramics, or glassy materials. Ceramics and glasses conduct ions better than polymers, while ceramics have the added benefit of being more flexible and not brittle. Finding the right balance of properties is difficult, however. As Mitch Jacoby points out in a *C&EN* story on fire-resistant batteries, "modifying a solid to boost its ionic conductivity via chemical treatment or other means could make it more difficult to process, less stable electrochemically, or more expensive."[54] In that *C&EN* story, Jacoby highlights several research efforts on glass-ceramic lithium-ion conductors that are either oxide or sulfide compounds. Among this research is a lithium-doped glass electrolyte developed by lithium battery pioneer John Goodenough.[55] This battery uses a lithium metal anode and the new electrolyte has twice the energy density of conventional lithium-ion batteries and lasts through 23,000 recharge cycles.



Schematic representation of the charge process. The active particle on the right side represents a hypothetical charge on a particle. While charging, electrons and Li ions leave the active particles. While ions accumulate at the surface with the plasticizer, the electrons are transported through the carbon and current collector to the external circuit.

Reprinted in part by: *J. Am. Chem. Soc.*, 2018, *140* (20), pp 6343–6352

DOI: 10.1021/jacs.8b02322

Publication Date (Web): April 24, 2018

Solid-state battery technology has garnered immense excitement from investors and large corporations. Toyota, Honda and Nissan have teamed up with Panasonic to develop solid-state batteries for electric vehicles. Experts predict that the solid-state battery might become commercially available by 2020 and start being implemented in cars by 2025. Several startups are now in the test and validation phases of their prototypes. Ionic Materials has raised $65 million from major investors for its patented plastic electrolyte that they say boosts energy density and lowers cost. Others, such as Blue Current are pursuing a hybrid polymer-ceramic electrolyte that combines the best of both materials. SolidEnergy Systems in Massachusetts uses a mixed polymer-ceramic electrolyte at its lithium metal anode and a paste of lithium salts on the cathode. The company has doubled the energy density of conventional lithium ion, and plans to sell its semi-solid battery for drones and wearable electronics. Meanwhile, Solid Power has made a battery with a lithium metal anode, a conventional cathode, and a solid electrolyte made of lithium, sulfur, and phosphorus.[56] The startup has a partnership with BMW to develop solid-state batteries for electric vehicles and has raised $20 million from Samsung and Hyundai to complete a manufacturing facility for its battery.

Lithium-Sulfur

To boost the energy that lithium batteries can deliver, efforts continue on making cathodes and anodes that can hold more charge. The lithium-sulfur battery has evolved from such efforts. It has the potential of being more energy-dense and low-cost than conventional lithium-ion. Lithium-sulfur batteries are very different from conventional lithium-ion. Instead of having lithium ions flowing through the electrolyte without reacting with it, the lithium in the electrolyte reacts and forms chemical compounds. Conventional lithium-sulfur cells contain a pure lithium metal anode, a liquid electrolyte, and a cathode made of sulfur embedded in porous, conductive carbon. Its advantages are that sulfur is cheap and plentiful, and it has a very high theoretical capacity to hold charge. The battery's chemistry, which is based on lithium ions reacting reversibly with sulfur to form lithium sulfide, could theoretically allow cells to store five times as much energy per kilogram as conventional lithium-ion's 200 Wh/kg. However, the reaction also creates intermediate polysulfide compounds that dissolve in the electrolyte. This dilutes the electrolyte and degrades the cathode, and after a few hundred charge-discharge cycles the battery becomes unstable.

New advances coming from academic labs and some startups are starting to bring lithium-sulfur batteries to market.[57] The goal of most of this work is to reduce the polysulfide formation and dissolution of the sulfur at the cathode. Some researchers have replaced the porous carbon with graphene, the two-dimensional flexible carbon sheets that are electrically conductive and mechanically strong. A group at Lawrence

Berkeley National Laboratory made such sulfur-graphene composite electrodes with a protective coating that had an energy density of 500 Wh/kg and lasted around 1500 charging cycles.[58] Other approaches include encapsulating sulfur in carbon or polymer nanotubes, or to apply polymer coatings to carbon-sulfur structures.[59]

A variety of sulfur-polymer hybrid materials have also been developed. Electrodes made of sulfur embedded in conductive polymer networks have shown promise, with one group reporting batteries that survived 500 charge cycles.[60] Yet others are tinkering with the electrolyte. Linda Nazar and colleagues at the University of Waterloo have designed electrolytes that don't dissolve polysulfides.[61] Ionic liquid electrolytes have shown promise, and some groups are developing solid-state polymer electrolytes.

Lithium-sulfur batteries are most likely to enter markets where low weight is a critical need.[62] Better power and cycle life will be needed to break into other markets like satellite, aerospace and automotive. One startup is already moving ahead with commercialization. In 2018, UK-based Oxis Energy began manufacturing its lithium-sulfur batteries at a plant in Brazil. The batteries, which have a lithium anode and sulfur-based cathode, will debut in electric scooters sold in China, and the company then plans to develop them for drones and soldier's power packs.[63] Meanwhile, Sion Power in Tucson, AZ which received $50 million from chemical company BASF in 2012, has shelved its lithium-sulfur research and switched instead to developing lithium-metal batteries.[64]

Metal-Air

Metal-air batteries could, in theory, store significantly more energy than lithium-ion. These batteries have a metal anode and a cathode made of pure oxygen infused into a porous carbon support. Many different metals have been investigated for potential use: aluminum, lithium, sodium, tin, and zinc. Lithium-air could theoretically store 13,000 Wh/kg — matching the energy density of gasoline — for less cost and weight than lithium-sulfur. Aluminum-air has a slightly lower energy density of 8,000 Wh/kg.[39]

Lithium-air batteries boast an exciting combination of power, weight and cost, according to a 2015 article in the journal *Nature*.[28] The battery was first proposed in the 1970s for automotive uses. It has received renewed attention and hype in recent years as the ideal low-cost, low-weight battery for electric vehicles. Cells made until now have used the same organic electrolytes as those in conventional lithium-ion batteries. Issues with the metal anode, air cathode, and electrolyte have kept it from fulfilling its full potential, and the technology is estimated to be ten years away from commercialization. Despite the word air in its name, the battery cathode needs pure oxygen, which would require systems to purify, pump and store air. During discharge, oxygen reacts with lithium ions to form lithium oxides. But the oxygen and the lithium oxides can also react with the electrolyte, consuming it. The reaction also creates a film of insulating lithium peroxide on the cathode, which prevents electron movement. This reduces the battery's storage capacity and makes it difficult to recharge. These unwanted reactions cut battery life short; lab prototypes currently only last for 50 cycles.

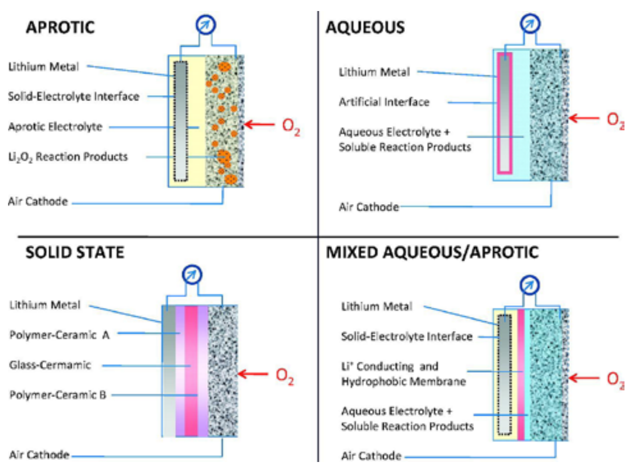
Experts have outlined a series of challenges that need to be solved before lithium-air batteries can be commercialized.[65] These include:

- the development of a stable, oxidation-resistant electrolyte
- air-breathing membranes that separate oxygen from ambient air in order to avoid moisture, carbon dioxide, and other environmental contaminants from reaching the cathode and limiting the lifetime of the the batteries
- robust lithium metal or lithium composite electrode capable of repeated cycling at higher current densities
- additives, encapsulation or other systems to keep the insulating dilithium oxide from completely coating the cathode

The advantage of using metals such as zinc and magnesium is that they are much more plentiful than lithium.[66] These metals also work with an aqueous electrolyte. Rechargeable zinc-air batteries are now being seriously pursued for electric vehicles and grid storage.

Challenges facing these batteries are mostly at the metal anode.

Four Types of Li-Air Batteries



Four different architectures of Li–air batteries, which all assume the use of lithium metal as the anode. The three liquid electrolyte architectures are aprotic, aqueous, and a mixed aprotic–aqueous system. In addition, a fully solid state architecture is also given. Principal components are as labeled in the figure. Spontaneously occurring SEIs on the lithium anode are given as dashed lines, while artificial SEIs are given as solid lines.

Reprinted in part by: *Phys. Chem. Lett.*, 2010, *1* (14), pp 2193–2203

DOI: 10.1021/jz1005384

Publication Date (Web): July 2, 2010

The metal can corrode and also dissolves unevenly in the electrolyte. Uneven metal deposits on the anode during charge can also cause dendrites. This makes the battery unstable after a few charging cycles. Alloying zinc with other metals such as lead, cadmium and indium or introducing additives such as metal oxides and organic acids can stabilize the zinc anode, but only to some extent. No such remedy has been found for aluminum-air and magnesium-air batteries yet.

NantEnergy (formerly Fluidic Energy) in Scottsdale, Arizona seems to have overcome the challenges of a zinc anode.[67] It has been selling zinc-air batteries for five years now to customers in developing nations. The batteries replace lead-acid systems and diesel generators for backup power in remote locations such as villages in Africa and Asia, and cellphone towers worldwide. The company claims its technology costs $200–300/kwh,[68] and that it has sold 100,000-plus batteries in 10 countries.

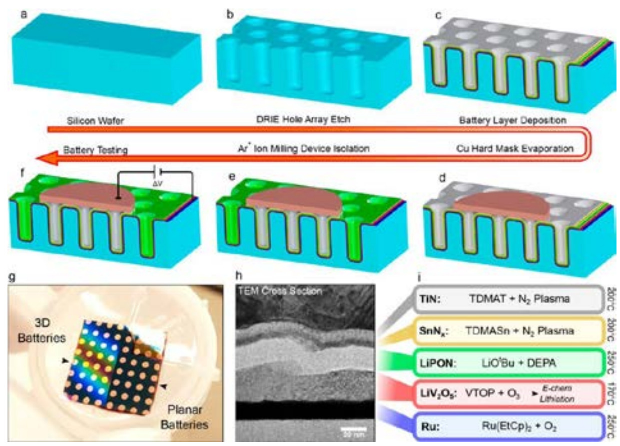
Flexible Thin-Film Batteries

The rising wave of wearable electronics, chip cards, tiny sensors for the "Internet of Things", and compact medical devices calls for batteries with very different traits than those for electric vehicles and grid storage. These devices require ultra-light, compact batteries that deliver low power but last for a long time. New materials, chemistries and manufacturing techniques are transforming batteries and have given rise to many thin, flexible battery technologies.[69]

Thin-film batteries are a type of solid-state battery made by stacking battery components that are each films a few micrometers thick. The complete battery cells are usually a few hundred micrometers thick, which makes them bendable. The layers are typically deposited using sputtering techniques. But they can also be printed or sprayed on, allowing for the batteries to be made using low-cost roll-to-roll techniques. Thin-film batteries are currently commercially available. A common approach to commercialization is to adapt conventional solid-state lithium-ion chemistry that uses solid polymer electrolytes. STMicroelectronics sells a paper-thin (0.25mm thickness) battery called EnFilm that has a lithium metal anode, lithium cobalt oxide cathode, and a lithium phosphorus oxynitride ceramic electrolyte. BrightVolt coats its polymer electrolyte directly on the electrodes to make a lightweight cell that is less than 0.5-mm thick. The electrolyte also acts as a glue to hold the battery components together.

Some companies are foregoing lithium in these batteries. Imprint Energy has swapped lithium for zinc and is making thin-film zinc-carbon batteries. The batteries use a new, stable chemistry for the electrolyte solution. They are screen-printed using the same equipment and methods used to print t-shirt designs. The result is a bendable, inexpensive device, the company says.

Several investigators are exploring 3D architectures for thin-film rechargeable battery electrodes. Bumpy or spiky electrodes would have more volume per unit area and thus hold more charge, boosting energy density. In a recent study, researchers reported a novel silicon-based 3D thin-film battery that is easy to make using common silicon-processing techniques.[70] The researchers make an anode by etching silicon pillars into a silicon wafer, coat it with a thin polymer electrolyte, and then fill the spaces between the pillars with a slurry of conventional nickel-based cathode material. The result is a battery with interlocking Lego-like electrodes separated by the electrolyte. Another group did something similar: they deposited all the battery layers one by one into an array of deep pores that were etched into silicon wafers.[71]

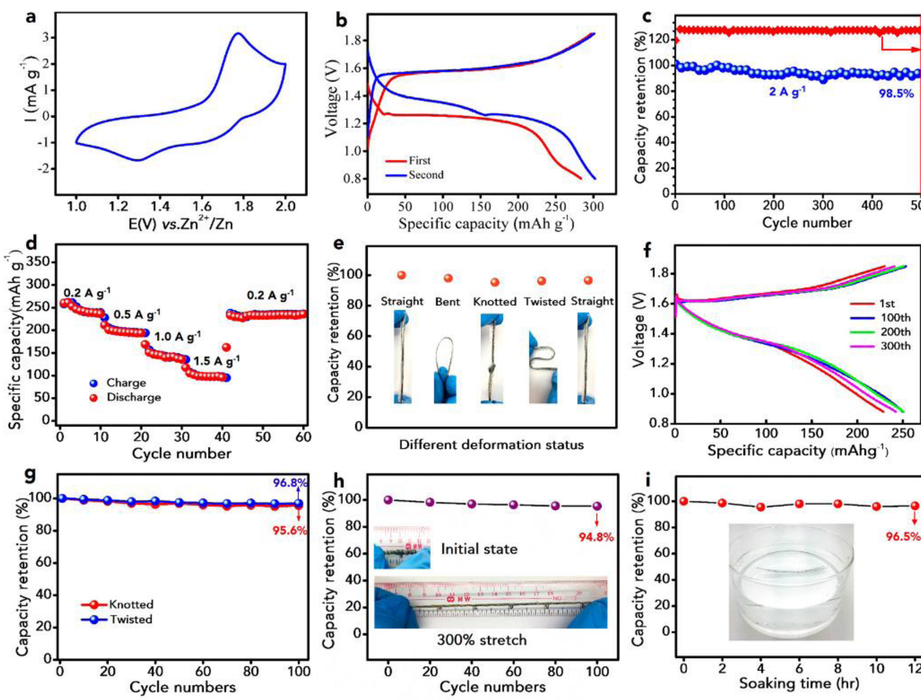


Fabrication and characterization of 3D solid-state thin-film batteries. (a–d) Schematic of fabrication of devices. (a) The silicon starting substrate. (b) Formation of cylindrical pore arrays via photolithographic patterning and DRIE of Si. Pores are 3 μm wide and either 12 (AEF 4) or 30 (AEF 10) μm in depth. (c) Blanket deposition of five active device layers via ALD, including electrochemical lithiation of the cathode as discussed in the text. (d) Deposition of Cu through a shadow mask to form 1 mm diameter circular dual purpose etch mask/needle probe contacts. (e) Isolation of individual batteries via Ar^+ ion milling through anode current collector and anode films. (f) Battery testing through contact with top electrode and cathode current collector layers. (g) Optical photograph of finished battery “chip”. Each chip is dual sided, with 3D batteries on the left and planar batteries on the right. Optical iridescence from the 3D array causes the visible coloration. (h) Cross-sectional TEM image of an all-ALD solid-state battery with 40 nm Ru/70 nm LiV_2O_5/50 nm Li_2PO_2N/10 nm SnN_x/ 25 nm TiN. (i) Overview of ALD chemistry and process temperature for each layer visible in (h).

Reprinted in part by: *ACS Nano*, 2018, *12* (5), pp 4286–4294
DOI: 10.1021/acsnano.7b08751
Publication Date (Web): April 24, 2018

Additive manufacturing, also known as 3D printing, could revolutionize how thin batteries are made.[72] It would allow 2D or 3D batteries to be printed using different inks in a layer-by-layer manner, where each layer can be plastic, metal or another material. While the technique is expensive now, its costs are going down and it could lead to batteries being made on a large scale at a very low cost.

Yarn or fiber-shaped batteries are yet another exciting area of research.[73] Small and flexible, they could be woven directly into textiles to power electronics and medical implants. Carbon fibers are the foundation of yarn batteries made by many groups.[74,75] The idea is to coat one carbon fiber with anode material and another with cathode material, and then twist them together to make a yarn. Using this design, researchers in Hong Kong made a rechargeable zinc-manganese battery that was stretchable and that worked even when cut, knotted and washed.[76]



Electrochemical performance of the rechargeable yarn ZIB (zinc ion battery). (a) CV curve at a scan rate of 2 mVs^{-1}. (b) Initial two discharge/charge curves at a current density of 60 mA g^{-1}. (c) Long-term cycling performance and Coulombic efficiency at 2 A g^{-1}. (d) Rate capabilities at various current densities. (e) Capacity retention of the yarn ZIB under various deformation status. (f) Discharge curves of the yarn ZIB after different bending cycles. (g) Capacity retention of the yarn ZIB under knotted and twisted conditions. (h) Dependence of capacity retention on cycle numbers with a strain of 300%. (i) Capacity retention test of the yarn ZIB for 12 h continuous underwater immersion in DI water at 24 °C, showing superior waterproof ability. For (e–i), tests were performed at a current density of 0.3 A g^{-1}.

Reprinted in part by: *ACS Nano*, 2018, *12* (4), pp 3140–3148

DOI: 10.1021/acsnano.7b09003

Publication Date (Web): March 28, 2018

Another study reports a lithium battery made by twisting two carbon nanotube composite yarns on a cotton fiber: a carbon nanotube/silicon yarn anode and a carbon nanotube-lithium manganite cathode.[74] Another team has used a different approach: metal springs or spirals instead of carbon fibers as the backbone for battery components.[77] Such wire batteries are more resilient to fatigue. The design could work with different material combinations, and the team demonstrated a silver-zinc system.

There are also silver-zinc, aluminum-air and zinc-air yarn batteries currently being explored.[78,79,80] Researchers and battery firms regularly reveal new thin-film and fiber battery designs. The thin-film battery market is expected to explode in coming years and should be worth $1.72 billion by 2025, according to a recent report.[81]

VII. CONCLUSION

Reliance on battery-powered devices bring daily frustrations like phones draining much too quickly, or *range* anxiety, the fear of not reaching the next car-charging station before the EV's battery runs out. But rechargeable batteries have made leaps and bounds since they were first invented. Lithium-ion and lead-acid batteries are inescapable parts of modern life, and will be for quite some time to come, even with the significant advances that have been made to date. Chemists, engineers, and materials scientists continue to pursue better battery technologies. While some are focused on advancing lithium-ion chemistry, others are preparing for a post-lithium world with completely new technologies. These advances offer hope that batteries will keep getting more powerful, long-lived, lightweight, and affordable. As these improved energy-storing devices continue to improve they will support and complement the ongoing smart, miniaturized electronics revolution and could enable a transition to renewable energy and pollution-free transportation.

VIII. REFERENCES

(1) John B. Goodenough and Kyu-Sung Park. "The Li-Ion Rechargeable Battery: A Perspective." *Journal of the American Chemical Society* 2013, 135 (4): 1167-1176.

(2) James Manyika and Michael Chui. "Better Batteries, Better World." 2013; available online at https://www.foreignaffairs.com/articles/united-states/2013-08-11/better-batteries-better-world.

(3) "In search of the perfect battery." 2008; available online at https://www.economist.com/technology-quarterly/2008/03/06/in-search-of-the-perfect-battery.

(4) "The Octagon Battery — What Makes a Battery a Battery." available online at https://batteryuniversity.com/learn/article/the_octagon_battery_what_makes_a_battery_a_battery.

(5) Battery Recycling as a Business; available online at https://batteryuniversity.com/learn/article/battery_recycling_as_a_business.

(6) Grand View Research. "Lead Acid Battery Market Size & Trend Analysis." 2017; available online at: https://www.grandviewresearch.com/press-release/global-lead-acid-battery-market.

(7) Frost & Sullivan. "Global Analysis of Battery Materials Market, Forecast to 2023." 2018; available online at https://www.prnewswire.com/news-releases/li-ion-and-lead-acid-battery-applications-push-global-battery-materials-market-toward-43-2-billion-by-2023--300647505.html.

(8) Bloomberg NEF. "Electric Vehicle Outlook 2018." 2018; available online at https://about.bnef.com/electric-vehicle-outlook/.

(9) Christoph Rauwald. "VW to Build Electric Versions of all 300 Models by 2030." 2017; available online at https://www.bloomberg.com/news/articles/2017-09-11/vw-ceo-vows-to-offer-electric-version-of-all-300-models-by-2030.

(10) Sean O'Kane. "Three US States will spend $1.3 billion to build more electric vehicle charging." 2018; available online at https://www.theverge.com/2018/6/1/17416778/california-new-york-electric-charging-investment-stations.

(11) Wikipedia. Grid Energy Storage. available online at https://en.wikipedia.org/wiki/Grid_energy_storage#Batteries.

(12) USA News Group. "South Korea Takes Lead in Lithium Power Battery Supremacy." 2018; available online at https://www.prnewswire.com/news-releases/south-korea-takes-lead-in-lithium-power-battery-supremacy-670506423.html.

(13) Julian Spector. "Tesla Fulfilled Its 100-Day Australia Battery Bet. What's That Mean for the Industry?" 2017; available online at https://www.greentechmedia.com/articles/read/tesla-fulfills-australia-battery-bet-whats-that-mean-industry.

(14) California Energy Commission – Tracking Progress. 2018; available online at http://www.energy.ca.gov/renewables/tracking_progress/documents/energy_storage.pdf.

(15) Chris Martin. "Better Batteries." 2018; available online at https://www.bloomberg.com/quicktake/batteries.

(16) Lead Acid Systems; available online at https://batteryuniversity.com/learn/archive/advancements_in_lead_acid.

(17) https://batteryuniversity.com/index.php/learn/article/new_lead_acid_systems.

(18) Anjan Banerjee et al. "Single-Wall Carbon Nanotube Doping in Lead-Acid Batteries: A New Horizon." *ACS Applied Materials & Interfaces* 2017, 9 (4): 3634-3643.

(19) Hai-Yan Hu et al. "Enhanced Performance of E-Bike Motive Power Lead–Acid Batteries with Graphene as an Additive to the Active Mass." *ACS Omega* 2018, 3 (6): 7096-7105.

(20) International Lead Association. Lead Uses – Statistics; available online at https://www.ila-lead.org/lead-facts/lead-uses--statistics

(21) Battery Council International. "National Recycling Rate Study." 2017; available online at https://cdn.ymaws.com/batterycouncil.org/resource/resmgr/Recycling_Rate/BCI_201212-17_FinalRecycling.pdf.

(22) Tullo, A. H. "Battery recyclers get the lead out." *C&EN* 2018, 96 (6); available online at https://cen.acs.org/articles/96/i6/Battery-recyclers-lead.html.

(23) Nickel-based Batteries; available online at https://batteryuniversity.com/learn/article/nickel_based_batteries.

(24) Global Battery Markets; available online at https://batteryuniversity.com/learn/article/global_battery_markets.

(25) Arumugam Manthiram. "An Outlook on Lithium Ion Battery Technology." *ACS Central Science*, 2017, *3* (10): 1063-1069.

(26) Kathie Zipp. "Trending in solar storage: Flow battery storage improving but lithium-ion still rules." 2017; available online at https://www.solarpowerworldonline.com/2017/06/trending-solar-storage-flow-battery-technology-improving-lithium-ion-still-rules/.

(27) Lithium-based Batteries; available online at https://batteryuniversity.com/learn/article/lithium_based_batteries.

(28) Eric C. Evarts. "Lithium batteries: To the limits of lithium." 2015, *Nature*, 526: S93–S95.

(29) Kevin Clemens. "Funding for Advanced Battery Research Hangs in Balance." 2018; available online at https://www.designnews.com/electronics-test/funding-advanced-battery-research-hangs-balance/209620887059076.

(30) The Faraday Institution 2018; available online at https://faraday.ac.uk/the-faraday-institution-announces-42-million-for-energy-storage-research/.

(31) Prachi Patel. "Improving the Lithium-Ion Battery. *ACS Cent. Sci.*, 2015, 1 (4): 161–162.

(32) James Attwood and Martin Ritchie. 2018; "Elon Musk Warns That Tesla's Cobalt Use Is Heading Towards Zero." 2018; available online at https://www.bloomberg.com/news/articles/2018-05-02/tesla-supercharging-its-model-3-means-less-cobalt-more-nickel.

(33) Yang-Kook Sun et al. "Cobalt-Free Nickel Rich Layered Oxide Cathodes for Lithium-Ion Batteries." *ACS Appl. Mater. Interfaces*, 2013, *5* (21): 11434–11440.

(34) Michael McCoy. "Matthey advances lithium nickel oxide battery material." *C&EN* 2018, 96 (29).

(35) Kostiantyn Turcheniuk et al. "Ten years left to redesign lithium-ion batteries." *Nature* 2018, 559: 467-470.

(36) Fathy M. Hassan et al. "Subeutectic Growth of Single-Crystal Silicon Nanowires Grown on and Wrapped with Graphene Nanosheets: High-Performance Anode Material for Lithium-Ion Battery." *ACS Appl. Mater. Interfaces*, 2014, *6* (16): 13757–13764.

(37) Sichang Guo et al. "Tunable Synthesis of Yolk–Shell Porous Silicon@Carbon for Optimizing Si/C-Based Anode of Lithium-Ion Batteries." *ACS Appl. Mater. Interfaces*, 2017, *9* (48): 42084–42092.

(38) Shiqiang Huang et al. "Nanostructured Phosphorus Doped Silicon/Graphite Composite as Anode for High-Performance Lithium-Ion Batteries." *ACS Appl. Mater. Interfaces*, 2017, 9 (28): 23672–23678.

(39) Experimental Rechargeable Batteries; available online at https://batteryuniversity.com/index.php/learn/article/experimental_rechargeable_batteries.

(40) Evan M. Erickson*, Chandan Ghanty, and Doron Aurbach "New Horizons for Conventional Lithium Ion Battery Technology." *J. Phys. Chem. Lett.*, 2014, *5* (19): 3313–3324.

(41) Prachi Patel. "Fire-retardant electrolyte could usher in practical lithium metal batteries." 2018; available online at https://cen.acs.org/energy/energy-storage-/Fire-retardant-electrolyte-usher-practical/96/web/2018/06.

(42) Kai Liu et al. "Materials for lithium-ion battery safety." *Sci. Adv.* 2018, 4 (6): eaas9820.

(43) Biran H. Shen et al. "Shear Thickening Electrolyte Built from Sterically Stabilized Colloidal Particles." *ACS Appl. Mater. Interfaces*, 2018, *10* (11): 9424–9434.

(44) Patel, P., & Gaines, L. "Recycling Li batteries could soon make economic sense." *MRS Bulletin* 2016, 41(6)" 430-431.

(45) Elsa A. Olivetti et al. "Lithium-Ion Battery Supply Chain Considerations: Analysis of Potential Bottlenecks in Critical." *Joule* 2017, 1 (2): 229-243.

(46) Molicel; available online at http://www.molicel.com/hq/about/aboutus1.html.

(47) Katherine Bourzac, "IBM Invests in Battery Research." 2009; available online at https://www.technologyreview.com/s/413786/ibm-invests-in-battery-research/.

(48) Xin-Bing Cheng et al. "Nanodiamonds suppress the growth of lithium dendrites." *Nature Communications* 2017, volume 8: 336.

(49) Yayuan Liu et al. "An Ultrastrong Double-Layer Nanodiamond Interface for Stable Lithium Metal Anodes." *Joule* 2018, 2 (8): 1595-1609.

(50) Mitch Jacoby. "Nanodiamonds reduce short-circuit risk in rechargeable lithium batteries ." *C&EN* 2018, 95 (35): 6.

(51) Tuo Wang et al. "Ultrafast Charging High Capacity Asphalt–Lithium Metal Batteries." *ACS Nano*, 2017, 11 (11): 10761–10767.

(52) Lu Li et al. "Self-heating–induced healing of lithium dendrites." *Science*, 2018, 359 (6383): 1513-1516.

(53) Akshat Rathi. "The next major innovation in batteries might be here." 2018; available online at: https://qz.com/1349245/the-next-major-innovation-in-batteries-might-be-here/.

(54) Mitch Jacoby. "New materials for fire-resistant batteries." *C&EN Global Enterprise*, 2016, 94 (45): 30-32.

(55) Maria Helena Braga et al. "Nontraditional, Safe, High Voltage Rechargeable Cells of Long Cycle Life." *Journal of the American Chemical Society* 2018, *140* (20): 6343-6352.

(56) Akshat Rathi. "Solid Power raises $20 million in the race to build all-solid-state batteries." 2018; available online at: https://qz.com/1383884/a-startup-promising-an-all-solid-state-rechargeable-battery-has-raised-20-million/.

(57) Arumugam Manthiram et al. "Rechargeable Lithium–Sulfur Batteries." *Chem. Rev.*, 2014, *114* (23): 11751–11787.

(58) Min-Kyu Song, Yuegang Zhang, and Elton J. Cairns. "A Long-Life, High-Rate Lithium/Sulfur Cell: A Multifaceted Approach to Enhancing Cell Performance." *Nano Lett.*, 2013, *13* (12): 5891–5899.

(59) Scott Evers and Linda F. Nazar. "New Approaches for High Energy Density Lithium–Sulfur Battery Cathodes." *Accounts of Chemical Research* 2013 *46* (5): 1135-1143.

(60) Lifen Xiao et al. "A Soft Approach to Encapsulate Sulfur: Polyaniline Nanotubes for Lithium-Sulfur Batteries with Long Cycle Life." *Advanced Materials* 2012, 24 (9): 1176-1181.

(61) Mitch Jacoby. "New electrolyte improves Li-S batteries." *C&EN* 2018, 96 (33).

(62) Tom Cleaver et al. "Perspective — Commercializing Lithium Sulfur Batteries: Are We Doing the Right Research?" *J. Electrochem. Soc.* 2018, 165 (1): A6029-A6033.

(63) Alex Scott. "Lithium-sulfur to power e-scooter." *C&EN Global Enterprise* 2016, *94* (25): 12-13.

(64) Alex Scott. "Sulfur-based battery firms secure cash." *C&EN* 2018, 96 (10): 8.

(65) G. Girishkumar et al. "Lithium–Air Battery: Promise and Challenges." *The Journal of Physical Chemistry Letters* 2010, 1 (14): 2193-2203.

(66) Yanguang Li and Jun Lu. "Metal–Air Batteries: Will They Be the Future Electrochemical Energy Storage Device of Choice?" *ACS Energy Letters* 2017, *2* (6): 1370-1377.

(67) Eric Wesoff. "Fluidic Energy Is the Biggest Zinc-Air Battery Startup You Haven't Heard Of." 2015; available online at: https://www.greentechmedia.com/articles/read/fluidic-energy-is-the-biggest-zinc-air-battery-startup-you-havent-heard-of.

(68) BloombergNEF 2017; available online at: https://about.bnef.com/blog/new-energy-pioneers-fluidic-energy

(69) Gary Marshall. "Lights of the charge brigade: Batteries that will give wearables stamina and style." 2015; available online at: https://www.wareable.com/wearable-tech/batteries-that-will-give-wearables-stamina-and-style-1223.

(70) Janet I. Hur, Leland C. Smith, Bruce Dunn. "High Areal Energy Density 3D Lithium-Ion Microbatteries." *Joule* 2018, 2 (6): 1187–1201.

(71) Alexander Pearse et al. "Three-Dimensional Solid-State Lithium-Ion Batteries Fabricated by Conformal Vapor-Phase Chemistry." *ACS Nano* 2018, 12 (5): 4286-4294.

(72) Corie L. Cobb and Christine C. Ho. "Additive Manufacturing: Rethinking Battery Design." The Electrochemical Society *Interface* 2016; available online at: http://interface.ecsdl.org/content/25/1/75.full.pdf.

(73) Zhaowei Xi et al. "Recent Progress in Flexible Fibrous Batteries." *ChemElectroChem* 2018, 5 (21): 3127-3137.

(74) Wei Weng et al. "Winding Aligned Carbon Nanotube Composite Yarns into Coaxial Fiber Full Batteries with High Performances." *Nano Letters* 2014, *14* (6): 3432-3438.

(75) Kai Wang et al. "High-Performance Cable-Type Flexible Rechargeable Zn Battery Based on MnO2@CNT Fiber Microelectrode." *ACS Applied Materials & Interfaces* 2018 *10* (29): 24573-24582.

(76) Hongfei Li et al. "Waterproof and Tailorable Elastic Rechargeable Yarn Zinc Ion Batteries by a Cross-Linked Polyacrylamide Electrolyte." *ACS Nano* 2018, *12* (4): 3140-3148.

(77) Alla M. Zamarayeva et al. "Flexible and stretchable power sources for wearable electronics." *Science Advances* 2017, 3 (6): e1602051.

(78) Jae Myeong Lee et al. "Biscrolled Carbon Nanotube Yarn Structured Silver-Zinc Battery." *Sci. Rep.* 2018, 8: 11150.

(79) Joohyuk Park et al. All-Solid-State Cable-Type Flexible Zinc–Air Battery. *Advanced Materials* 2014, 27 (8): 1396-1401.

(80) Yifan Xu et al. "An All-Solid-State Fiber-Shaped Aluminum–Air Battery with Flexibility, Stretchability, and High Electrochemical Performance." *Angewandte Chemie* 2016, 128 (28): 8111-8114.

(81) Grand View Research. "Global Thin-Film Battery Market." 2018; available online at https://www.grandviewresearch.com/press-release/global-thin-film-battery-market.

ACS
Chemistry for Life®

AMERICAN CHEMICAL SOCIETY
1155 SIXTEENTH STREET, NW
WASHINGTON, DC 20036
www.acs.org