

High-energy battery technologies



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Introduction

Energy storage is crucial in ensuring society has access to a ready supply of sustainable electrical power, and is a fundamental enabler for sectors from transportation to consumer electronics. From the increased market uptake of electric vehicles to growing environmental concerns and legal mandates to shift away from fossil fuels, there has been a rapid rise in global demand for lithium-ion batteries. The global lithium-ion battery market is forecast to exceed \$73 billion by 2025, achieving a compound annual growth rate of 11 per cent¹.

As a result of increasing global demand and competition, batteries steadily have been getting better. It is more than two centuries since Michael Faraday's first recorded experiment, in which he stacked seven ha'penny coins, seven disks of sheet zinc, and six pieces of paper moistened with salt water to create a voltaic pile – a rudimentary precursor to the modern battery. It is 25 years since Sony released a commercial version of the rechargeable lithium-ion battery. Invented in the UK, it now sits snugly in countless smartphones, laptops and other devices. Rechargeable lithium-ion batteries still provide the best combination of compactness, power and efficiency for products ranging from drones to smartphones and cars, but research continues into alternatives that can improve performance in a number of areas, from energy density, to specific energy and cycle life (how many times a cell can be recharged before it needs replacing).

For those keen to explore new ways of electrifying their products and services this opens up enormous potential, but with it comes enormous complexity. Once limited, the battery landscape is now characterised by a greater choice of technology options. Further still, new technologies are in development or just emerging on the market with characteristics that may be well suited for some applications, but not others. For a technology company, making the wrong battery choice could be commercially catastrophic.

Understanding which battery options offer a given technology the greatest immediate promise, and which need more time to mature, is essential to a sector's commercial development process. To help organisations make critical electrical power decisions today to maximise the potential of their capabilities tomorrow, the Faraday Institution has developed this report, which considers the most promising technology developments in the field of high-energy batteries. By high-energy, we mean those with the capacity to store and deliver large amounts of energy, as opposed to high-power, which deliver energy quickly. High-energy batteries are designed to achieve aims such as enabling electric vehicles to drive farther on a single charge, or consumers to use their mobile devices longer between charges.

Alongside our assessment of current technical progress, the report offers an overview of the main applications for battery systems, the drivers for adoption for those applications, the most relevant battery technologies for each, as well as any applications where certain technologies are not suitable. By doing so, the report provides an accessible starting point for any company considering new battery systems for their products or services.

Our key metrics for energy content are:

- Energy density, or volumetric energy, defined as the battery's energy content in relation to its volume, usually measured in Watt-hours per litre (Wh/l); and
- Specific energy, or gravimetric energy, defined as the battery's energy content in relation to its mass, usually measured in Watt-hours per kilogram (Wh/kg).

This report includes details on emerging technologies and market values throughout. For easy reference this data is summarised in Appendix 1 and 2 on pages 32 and 33.

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Sectors and their energy requirements

Portable consumer electronics

Cast your mind back 20 years or so and you will remember a time when mobile phones were almost exclusively for calling people and sending the occasional text message. Consequently, they tended to be used intermittently, only when needed for communicating. The devices also required little computing power, meaning batteries could last for days between charges.

Fast-forward to the present day and usage habits have changed dramatically. A 2018 study by UK communications regulator Ofcom revealed the average time spent online on a smartphone is almost two and a half hours a day, rising to three hours and 14 minutes for 18 to 24-year-olds². The humble mobile phone has morphed into a constantly connected entertainment centre on which users can take photos, watch whole movies, play games and listen to music.

Smartphone developers are under pressure to provide all this additional functionality without compromising on operational battery life. A survey of 1,303 smartphone buyers for the USA Today newspaper in 2019 showed that consumers are far less concerned with innovations such as folding screens and 5G than they are with having a battery that lasts all day. In fact, 76 per cent of iPhone owners and 77 per cent of Android users cited longer battery life as a key factor in their purchasing decisions³. In a hotly contested market, where the products are often very similar, battery life may even be the differentiating factor that provides the competitive edge.

Smartphones: consumer demands

For a while, consumer preference trended toward smaller and smaller mobile devices, forcing developers to squeeze more energy out of ever-shrinking batteries. But then manufacturers were granted something of a reprieve, as devices began growing again to accommodate consumer demand for larger screens, providing more volume in which to house bigger batteries with more energy. However, phones may now have reached their optimum size; in the *USA Today* study, less than a third of respondents said they wanted a bigger screen, which will once again put pressure on developers to seek out batteries with greater energy density to service power-hungry apps and features.

Smartphones: industry demands

For mobile device designers, there are significant challenges in delivering the battery life the consumer wants without making the device bigger, without compromising on its overall quality, and without incurring high manufacturing costs that necessitate a choice between reducing profit margins or increasing prices to levels that may deter buyers.

Developers have identified clever solutions to the volume challenge, such as the realisation that lithium-ion batteries do not have to be a uniform shape, enabling bespoke batteries to be precisely formed around the device's internal components. However, this does create challenges of its own. The tight integration of the battery means it cannot easily be replaced, so the life of the whole phone is determined by that of the battery. Cycle life is therefore very important, the expectation being between 500 and 1000 charges before the battery is no longer usable and the device must be recycled or replaced.

Other types of devices

While smartphones are the most prevalent of portable consumer electronic devices (Pew Research places ownership at 76 per cent among adults in advanced economies⁴), they are by no means the only category enjoying a surge in popularity.

The global market for wearable tech, which includes products like fitness trackers, health monitoring devices and augmented reality glasses, is expected to be worth \$34bn in 2020, according to analyst CCS Insight. Some of these devices may be integrated into clothing fabrics, making fire safety critical. Historically, the types of small battery used to power body-worn devices like watches and hearing aids have not been rechargeable, but manufacturers are now exploring solutions such as flexible rechargeable batteries by adapting lithium-ion and zinc-carbon systems.

A 2017 survey by the Consumer Technology Association (CTA) found that more than half of US adults who own mobile technologies also own a portable power device with which to charge them⁵. Respondents commented that portable power devices were needed because the battery life in their mobile devices was not sufficient to satisfy their heavy usage requirements.

The safety factor

Not all priorities are led purely by consumer preferences. Battery safety does not significantly influence buying decisions – the 2017 CTA survey found that only 18 per cent of people considered it an important factor when buying a portable power device, perhaps because consumers expect that manufacturers deal with the risk on their behalf – so for manufacturers it is critical. The Samsung Galaxy Note 7 became a poster child for the potential dangers of lithium-ion batteries following a series of issues in 2016. A combination of manufacturing faults prompted a product recall, costing the company an estimated \$5.3bn⁶, and leading the US Transport Security Administration and a number of international airlines to ban the device from aircraft. Given the enormous potential monetary losses associated with incidents of this type, tech companies would be well advised to invest in research that could help prevent them from happening.

Key battery technologies for portable consumer electronics

- High-energy lithium-ion commercial cells Page 11
- Pre-commercial lithium metal rechargeable cells Page 14
- Nickel-rich cathodes Page 15
- Silicon anodes Page 18
- Solid-state batteries Page 24

Electric vehicles

In 2017, the UK Government made a commitment to ban the sale of petrol and diesel cars by the year 2040⁷. While campaigners have pushed for this deadline to be brought forward to 2030⁸, it's not just the Government they need to convince. Consumers have been slow to purchase electric vehicles (EV), citing 'range anxiety' as one of the main factors in their reluctance to buy despite the fact that in reality 99% of journeys are less than 100 miles.

Range anxiety, perhaps better referred to as charging anxiety, is the fear of running out of battery energy mid-journey and ending up stranded. A 2019 study by the Transport Research Laboratory (TRL), based on the real-world driving experiences of 200 test subjects, confirmed that the range of EVs remains a critical factor for

uptake for UK customers⁹. Another survey by Volvo in the US found that 'running out of power' was the number one fear among motorists about switching to electric, although purchase cost was also a major factor for 57% of respondents¹⁰. These fears must be allayed quickly if we are to expect 100 per cent consumer take-up within a decade or two.

What will it take to make people switch?

Public attitude challenges underline the need for energy-dense batteries that can increase vehicles' range, offering owners greater choice and flexibility in their driving and recharging routines. Part of the solution will be changing consumer perceptions, as there is a tendency for drivers – especially in cities – to overestimate the battery life needed in practice. Data from the UK's Department for Transport shows the average car journey in England in 2018 was just 6.6 miles¹¹. Investment in charging infrastructure will also be crucial, although making it work for everyone presents a host of challenges. Competition for on-street charging stations can be fierce in densely-populated urban areas where parking spaces are scarce. Residents living in flats above the ground floor are not able to run cables to their vehicles to charge them using their home supply. The introduction of public 'drop-in' charging hubs, akin to petrol stations, may help to improve accessibility, but will require car batteries to charge in a matter of minutes to be practicable. Greater energy density means greater range, which in turn means fewer visits to charging hubs. Both energy density and charge time are improving rapidly.

There is certainly cause for optimism. In the aforementioned TRL survey, 50 per cent of participants said they would use an electric vehicle as a main car if it could travel 200 miles on one charge, rising to over 90 per cent if it could travel 300 miles. Recent leaps in technology mean the electric vehicles currently rolling off production lines are approaching that figure. Tesla's Model S Long Range leads the field, claiming 373 miles, but models from Jaguar, Kia, Hyundai and Mercedes-Benz are already exceeding 250 miles.

Of course, range is not the only consideration in selecting the right battery technology for future electric vehicles. Safety is an important factor, as packing more and more energy into an ever smaller space could increase the chances of fire or explosion if sufficient safety control systems are not put in place to mitigate the added risk. The public perception of lithium-ion batteries as being unsafe has been a cause of contention, although this may be unjustified. A 2017 report for the US Department of Transportation concluded that:

"...the propensity and severity of fires and explosions from ... lithium-ion battery systems are anticipated to be somewhat comparable to or perhaps slightly less than those for gasoline or diesel vehicular fuels¹²."

However, the report acknowledges that more data is needed before the matter can be settled. Also, perception matters, so neither consumers nor manufacturers would turn away an even safer, high-performance, low-cost alternative if such a solution can be developed.

What is required of an electric vehicle battery?

The US Advanced Battery Consortium (USABC) has published a series of performance targets for electric vehicles. In its view, an electric vehicle battery should meet the following specifications:

- Useable Specific Energy at C/3 rate: 350 Wh/kg at cell level, 235 Wh/kg at pack level
- Useable Energy density at C/3 rate: 750 Wh/l at cell level, 500 Wh/l at pack level
- Peak specific discharge power (80% Depth of Discharge, 30s): 700 W/kg
- Peak power density (80% Depth of Discharge, 30s), 1500 W/l
- Cycle life: 1000 cycles

- Calendar life: 15 years

- Cost: \$100/kWh

No battery today meets all of these criteria. If the claims of US company Sion Power prove true¹³, its Licerion-branded lithium-metal rechargeable cell (page 14) may come closest, but for researchers investigating competing solutions there is still a lot to play for.

What is the best approach to date?

Most existing commercial EV batteries are based on lithium-ion chemistry, making it the benchmark against which all potential alternatives are measured. A 2018 EU Joint Research Centre (JRC) report on the future markets for Li-ion batteries identified the average battery capacity based on annual sales as being 39 kWh for a battery electric vehicle (BEV) and 11 kWh for hybrid electric vehicle (HEV). The main cathode chemistries cited in the report are nickel manganese cobalt (NMC) and nickel cobalt aluminium oxide (NCA).

Different EV manufacturers have taken a variety of approaches to battery system architectures. Tesla uses a large array comprising thousands of relatively small cylindrical cells. Initially, Tesla used mass-market 18650 cells, but is now using slightly larger 21700 cells. The 21700 cell is around 50 per cent larger by volume than the 18650 but Tesla claims it provides around 20 per cent more specific energy at a similar manufacturing cost. Other developers favour fewer, higher capacity prismatic cells. The casing of a large prismatic cell accounts for a smaller percentage of its total weight, so its specific energy can be higher. Prismatic cells also pack together more efficiently. Cylindrical cells have some advantage because they can be more easily tightly wound, reducing resistance in the cell. It is also easier to maintain compression in a cylinder than in a rectangular case but this gives other problems such as increased internal stress. Time will tell which format becomes the preferred solution but currently most manufacturers seem to be preferring a prismatic cell packaged in a pouch.

Near-future alternatives to lithium-ion batteries are likely to remain lithium-based, such as lithium-sulfur (Li-S) and other chemistries using lithium metal anodes. Li-S offers higher specific energy, but is poorer volumetrically. Low cycle life may also be an issue compared to lithium-ion. The potential benefit of sulfur is its low cost compared to other cathode materials. Lithium-metal based cells with intercalation cathodes, a more direct successor to conventional Li-ion, offers gains in both specific energy and energy density, hitting "range anxiety" head-on. Lithium-metal intercalation cells may well overtake Li-S, leaving it to fall by the wayside. Looking to the longer term, researchers are already looking at cheaper and more readily available metals that could eventually take lithium's place in the EV market.

Key battery technologies for electric vehicles

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Civil aviation

Although batteries have been used to power on-board systems in aircraft for decades, fully electrical powered flight is still in its infancy. The fact we do not yet see fleets of electric passenger airliners cruising quietly above

our heads is almost entirely due to the present-day limitations of power and energy provision. Aviation generally requires huge amounts of power to be delivered over prolonged periods of time, and today's battery technology is not capable of meeting the performance demands for long-haul aircraft in a package small and light enough to be conducive to flight.

That is not to say it will never happen. Industry experts place the introduction of the first large-capacity electric passenger aircraft at anywhere between 10 and 20 years from now, and there are certainly plenty of good reasons to try. Aviation accounts for two per cent of global greenhouse gas emissions, according to the International Civil Aviation Organization (ICAO)¹⁴. At a time of unprecedented urgency to take action to counter climate change, research into high-energy batteries may define the future of the aviation industry; and of the planet.

First steps

Progress toward large electric airliners will be incremental, and so manufacturers are starting small. US company Ampaire is set to begin testing its six-seat hybrid-electric design, based on a retrofitted Cessna 337, on commercial routes to Hawaii in 2019. The model comprises one conventional combustion engine and one electric motor powered by lithium-ion batteries and is currently the largest of its kind ever flown.

The race to scale this type of technology is well underway. British start-up Faradair hopes to certify its 18-seat Bio Electric Hybrid Aircraft (BEHA) for passenger operations by 2025. Meanwhile, Wright Electric in the US has partnered with airline operator EasyJet to develop a 150-seat, all-electric plane, which it hopes will rival existing 737-sized aircraft in providing short-haul trips of under 300 miles by 2027.

High-energy battery technology will be fundamental to achieving these goals and, to an even greater extent, making the next logical leap to electric long-haul commercial flight.

Vertical take-off and landing (VTOL)

As some electric aircraft developers seek to compete against the fossil fuel-powered airliners of today, others are exploring completely different avenues.

Electric vertical take-off and landing aircraft (eVTOL) aim to exploit the potential of all electric propulsion to provide inexpensive, quiet and environmentally friendly short-range transportation. There are many different designs under development, and the Vertical Flight Society classifies eVTOLs into a number of categories:

- Wingless: multi-copter designs that work like scaled-up versions of commercial off-the-shelf multi-rotor drones, capable of carrying small numbers of passengers. Examples include the E-Hang 184 and Volocopter 2X.
- Vectored Thrust: winged aircraft that take off vertically, then tilt or redirect the same propulsion system to generate forward thrust, like the Lilium Jet and minibus-sized Bell Nexus, unveiled at the CES 2019 trade show.
- Lift + Cruise: winged aircraft that feature separate mechanisms for taking off vertically and cruising forward at speed. ZeeAero, Aurora Flight Sciences and Kitty Hawk are all working on prototypes.
- Hoverbikes: the airborne equivalent of motorcycles. Malloy Aeronautics has produced a working hoverbike under a contract with the US Department of Defense.
- Electric Helicopters: conventional helicopter designs that use electric motors instead of combustion engines, like the Sikorsky Firefly.

All of these prototypes are assumed to use similar batteries to those found in electric vehicles to meet the rigorous power and energy requirements. The biggest challenge in all cases is supplying sufficient energy for extended

flight times, especially in those which do not have wings to assist in generating lift, or those for which space is particularly constrained, such as hoverbikes and other personal flying devices.

A recent NASA presentation gave a useable eVTOL specific energy target at pack level of 400 Wh/kg, equating to an estimated cell specific energy of around 600 Wh/kg. This is significantly higher than the EV target and more than double the present-day commercial state-of-the-art lithium-ion battery.

More electric aircraft

Putting to one side the exoticism of electrically propelled aircraft, it is possible to achieve gains in performance, operating cost, reliability and emissions in the nearer term by adapting aircraft already in service. The More Electric Aircraft (MEA) concept aims to use electricity for all aircraft systems that are not associated with propulsion – systems that are currently driven by combinations of secondary power sources such as hydraulic, pneumatic and mechanical. In addition to the already growing energy demands presented by everything from air conditioning to in-cabin entertainment systems, this will create a significant additional requirement. Airbus and Rolls-Royce have partnered on a solution in the form of the E-Fan X demonstrator, due to make its first flight in 2020. A Rolls-Royce gas turbine installed in the rear fuselage will provide energy to a two-megawatt electrical generator. The ability to store this energy will be the key to ensuring it can be delivered where and when it is needed.

Safety first

The MEA approach is not without its risks. The Boeing 787 Dreamliner is the most electric aircraft currently in service, with two alternators for each of its two engines generating 250 kW each. In January 2013, shortly after its introduction, the Federal Aviation Administration (FAA) ordered all US airlines to ground their 787s amid reports of overheating lithium-ion batteries. The aircraft were allowed to return to service in April of that year following implementation of additional measures to contain battery fires. The episode underlines the inherent risks associated with energy-dense lithium-ion batteries, and the case for examining safer alternatives for use in aviation.

Key battery technologies for aerospace

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Unmanned systems

The global market for unmanned aerial vehicles (UAV) is expected grow from \$25.59bn in 2018 to \$70.28bn in 2029, according to analysis from BIS Research, with potential applications spanning multiple sectors, including infrastructure, agriculture, transport and security.

In the maritime environment, the unmanned underwater vehicle (UUV) and unmanned surface vehicle (USV) markets are forecast to reach over \$5bn and \$1bn respectively by the early 2020s, driven largely by demand in the maritime security and offshore oil and gas industries.

The defence sector is likely to remain at the forefront of unmanned ground vehicle (UGV) technology, with the market predicted to reach \$7bn by 2025.

Each of these domains – air, maritime and land – poses unique energy challenges, which must be solved if unmanned technology is to live up to its promise.

Unmanned aerial vehicles

Extending battery life in UAVs (commonly known as drones) will be critical if some of the more ambitious proposals are to be realised. Take parcel delivery as an example. To achieve flight with a heavy package the drone must be able to attain high peak power, but must also be capable of sustaining effort for extended periods to deliver over long distances.

There are two potential routes for achieving the required range:

The first is to provide multiple localised charging points for delivery drones, so they are not required to cover large distances on a single charge. This approach prioritises the battery's cycle life over its energy density, as it must be able to withstand frequent charging.

The second approach favours energy density over cycle life, opting for the battery that enables the longest possible flight time between charges. This is likely to be greatly preferable from a logistics perspective, as it centralises operations and minimises the charging cycle for the whole fleet. A minimum flight time of one hour may be necessary to support this method – or even three to four hours, depending on the area covered.

Unmanned maritime vehicles

The various options for alternative energy sources on board unmanned surface vehicles (USVs) reduce the importance of specific energy for propulsion – solar, wind and wave-powered surface craft can already operate continuously for weeks or even months at a time, while larger vehicles have the option of generating power using traditional fuels. The main role of the battery on a USV is therefore to power its payloads, such as sensors and communications equipment, along with providing the occasional added burst of propulsion. For many solutions, the battery will form part of a hybrid system, collecting and storing energy produced by solar or kinetic generators on board the craft, and so cycle life will be important.

Unmanned underwater vehicles (UUVs) are much more reliant on batteries than USVs, especially those required to operate at depth away from sunlight. The battery does not need to be light – in fact a heavy battery can actually be an advantage, as it adds ballast to help sink the craft. The major constraint is one of volume, as there is typically little room available on board. The ideal solution packs a lot of energy into a small space, and can tolerate extreme pressures and cold temperatures – but this may come at the cost of cycle life.

Unmanned ground vehicles

The technology used to power large unmanned ground vehicles (UGVs) will follow a similar trajectory to electric vehicles – starting with diesel hybrid systems before adopting emerging anode and cathode materials into their battery architectures.

In the military environment, small UGVs will present different challenges. Soldiers will carry the vehicles with them on the battlefield, so the batteries must not be so heavy or numerous as to limit their mobility. Safety and unit cost will be other key considerations, taking precedence over endurance or cycle life. The ideal battery will be small, light, and based on stable chemistry. It will either be quickly rechargeable, or low-cost enough to justify disposal after a single use – although the latter creates additional environmental considerations.

Bringing it all together

Many of the most promising applications for unmanned technologies will make use of multiple vehicles, working as whole systems that are not vulnerable to the loss of individual elements. As companies seek to assemble fleets of vehicles they will want bulk orders of safe, robust, low-cost, energy-dense batteries to power them. Economies of scale in manufacturing will reduce the unit cost per battery, but to achieve this, innovation must be shared to accelerate the pace of progress and prevent similar but incompatible technologies being developed in silos.

Key battery technologies for unmanned systems

- Lithium sulfur	Page 12
- Lithium metal rechargeable cells	Page 14
- Nickel-rich cathodes	Page 15
- Silicon anodes	Page 18
- Solid-state batteries	Page 24

Large-scale energy storage

Most of the requirements for high-energy batteries covered so far in this report have tended towards the very small, for applications in which space is constrained, but there is also a burgeoning market for large-scale battery installations. Research company Bloomberg New Energy Finance (BNEF) forecasts a rise from 9GW/17GWh in 2018 to 1,095GW/2,850GWh by 2040¹⁵, enabled by a steep drop in the cost of lithium-ion batteries. BNEF predicts that most of the new capacity will be utility-scale, although there will remain a strong market for home and business installations.

Sometimes referred to as Battery Energy Storage Systems (BESS), applications include energy storage for renewables, main grid, local microgrids and ship energy storage, where there is a large market for modular, often containerised energy storage in unit sizes of tens to hundreds of kWh scale.

A 2018 Joint Research Centre report considered lithium iron phosphate to be the dominant lithium-ion chemistry for large-scale storage¹⁶. Although it is a large market for lithium-ion batteries, it is not one in which high energy density or high specific energy are priorities, so there is good scope for exploring alternatives. Both lifetime (3000+ cycles) and cost are more important drivers, sometimes combined as a cost per cycle.

Energy storage for renewables

According to BNEF, more than half of electrical energy supplied to grids in large European economies will come from renewable sources by 2030. Storage will be fundamental in ensuring a successful transition from fossil fuels. Generation schemes that rely on natural energy sources, such as wind and solar farms, can only produce energy

under favourable conditions. For instance, a peak in energy usage between 5 p.m. and 7 p.m. may take place after sunset, depending on the country's latitude and the time of year. Since additional solar energy cannot be generated in response to the additional demand, the requirement must be met using stored energy previously generated during the daylight hours.

Improving continuity in existing grids

In August 2019 parts of England and Wales were hit by the biggest blackout in more than a decade, affecting nearly a million people. The outage had a significant impact on the London transport network, leaving passengers stranded at stations as train services were cancelled, and causing chaos on the roads as traffic lights went dark. The UK utility provider National Grid has indicated that a lighting strike may have caused the almost simultaneous loss of two large generators – one gas and one offshore wind. It was subsequently reported that National Grid had 1,000MW in reserve at the time, which was not enough to cover the 1,300MW capacity lost as a result of the outages. At the time of writing, investigations into the incident remain ongoing, so it cannot be said with certainty that greater battery storage would have prevented it. However, it does underline the cost and disruption that can result from such events, and large-scale energy storage undoubtedly has an important role to play in preventing similar outcomes in future. This will become even more relevant as the mass adoption of electric vehicles increases the transport network's dependency on power availability.

Home battery systems

Continuity may be further improved using domestic generation and storage. Such domestic storage solutions enable homeowners to become less reliant on the grid, making outages less likely and increasing society's resilience to outages if they do occur. The UK Government, as part of its Clean Growth Strategy, is providing incentives to homes and businesses to produce and store their own energy using renewable sources. Home energy generation is becoming a more attractive prospect for homeowners, as the cost of residential solar panels falls, dropping by 50 per cent since 2011. For domestic energy consumers, the switch to renewables could reduce bills by up to 30 per cent, while the government's Smart Export Guarantee provides the additional perk of being able to sell excess energy back to the grid.

Although energy density is still less important than cost and cycle life, it is likely to play a bigger role in home and business storage solutions than in utility-scale applications, as available space may be limited in domestic and workplace settings. Living and working alongside large high-energy batteries also makes safety an important consideration, providing a further incentive to consider alternatives to lithium-ion.

Key battery technologies for large-scale energy storage

- Nickel-rich cathodes Page 15
- Multivalent ion chemistries Page 26
- Aluminium-air Page 27

Technologies: part one

Current state-of-the-art

High-energy lithium-ion commercial cells

First patented in 1982, lithium-ion (Li-ion) has been the dominant battery technology since its discovery by John Goodenough at the University of Oxford and subsequent commercialisation by Sony and Asahi Kasei in 1991. Today's mobile phone industry would probably not exist without this technology, as its introduction doubled the energy density available to handheld devices compared to nickel-cadmium (NiCd) batteries.

Lithium-ion cells typically comprise a lithium cobalt oxide cathode and graphite anode, with a liquid electrolyte made up of lithium salts in a mix of organic solvents, although other new chemistries and electrode materials are pushing the boundaries of energy density, cycle life, and charge and discharge rate.

Advantages

Of the commercial battery technologies available today, Li-ion offers the best combination of energy density, longevity, versatility and affordability. The ability to pack so much energy into such a small space makes Li-ion the battery of choice for virtually every mobile electronic device. Over the years, the battery life of the average smartphone has steadily increased even as devices have become more power hungry, while the time taken to recharge them has significantly decreased.

Scaled up, these same qualities make Li-ion ideal for electric vehicles. The ability to travel long distances on a single quick charge is essential to gaining the support of consumers.

Its low mass and volume also make it ideal for lightweight applications like small unmanned aerial systems.

A low maintenance requirement further adds to its popularity. Li-ion battery self-discharge rate is low, starting at around five per cent in the first four hours after charging before falling to around one or two per cent per month. Unlike NiCd and similar batteries, it does not need to be regularly discharged to avoid the memory effect, in which the maximum energy capacity decreases with repeated charging.

Challenges

Safety is the greatest argument against the Li-ion battery. Its use of flammable electrolytes, stored under pressure, makes it susceptible to catching fire violently if pierced or crushed. Fires are also known to have been caused by short circuits and thermal runaway brought on by manufacturing faults or user error. There have been several high-profile examples of this in recent years. In 2016, Samsung discontinued production of its Galaxy Note 7 mobile device following a series of battery fires resulting from combinations of several different manufacturing faults. And in July 2019, a Virgin Atlantic flight from New York to London was forced to make an emergency landing at Boston when smoke and flames began emanating from a passenger seat. Upon inspection, bomb disposal experts discovered the remains of what appeared to be an external phone charger lodged between seat cushions.

Incidents like this make lithium-ion challenging for the airline industry, so while such incidents are rare, the successful commercialisation and proliferation of a safer alternative would make regulators breathe a huge sigh of relief.

Safety concerns do not rule out Li-ion for other applications. Tesla made headlines in April 2019 when one of its Model S electric vehicles suffered a battery fire in Shanghai. However, in response to the incident, the company

argued that its cars are around ten times less likely to catch fire than those powered by petrol. Common sense suggests that having a Li-ion battery on board is no riskier than driving around with 50 litres of highly combustible fossil fuel in the tank, even if fires associated with electric vehicles are more newsworthy. That said, safety is always a priority in the automotive industry, so the discovery of increasingly safer solutions is likely to be well received. Today's automotive batteries already have to pass stringent safety tests to ensure that they do not catch fire when crushed, punctured or heated in a fire.

Another disadvantage with Li-ion is that the limitations of the chemistry mean increases in energy density are becoming more incremental, having achieved annual performance improvements of only one or two per cent over the last five years. This slowdown means that investment in other emerging technologies may yield bigger returns as their progress begins to overtake that of Li-ion.

Development

Recent gains in performance of commercial cells have been achieved by exploring new materials for anodes and cathodes. Increasing amounts of silicon has been introduced to increase the capacity of graphite anodes and alternative higher capacity cathode materials such as lithium nickel cobalt aluminium oxide (NCA) and lithium nickel manganese cobalt oxide (NMC) are becoming more widespread. Cylindrical cells with NCA cathodes and silicon/graphite composite anodes, such as those used in the latest Tesla battery packs, have reached approximately 270 Wh/kg and 650 Wh/l.

The highest specific energy reported for a near-commercial lithium-ion cell is 304 Wh/kg, claimed by Chinese company Contemporary Amperex Technology Ltd (CATL). A development roadmap presented by CATL at the Advanced Automotive Battery Conference in 2017 suggests the cell is based on a silicon/graphite anode paired with a cathode comprising nickel, manganese and cobalt in a ratio of 8:1:1 (NMC811), rather than the NMC532 used in the company's current production cells. The same source projects 700 Wh/l for the technology. The battery is a flat prismatic design, unlike the cylindrical models used by Tesla. The prismatic format makes more effective use of space in the vehicle, but allowance must still be made for thermal management of cells.

Applications

- Mobile electronic devices Page 2
- Electric vehicles Page 3
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Pre-commercial lithium-sulfur cells

A lithium-sulfur (Li-S) cell is formed of a lithium metal anode coupled with a sulfur-based cathode. Although no such cell is currently available on a fully commercial, mass-market basis, companies such as Sion in the USA and Oxis in the UK do have niche commercial products and the technology was successfully used to power the *Zephyr* unmanned aerial vehicle (UAV), designed by QinetiQ and owned by Airbus, which holds the official endurance record for unrefuelled unmanned flight.

Advantages

Lithium-sulfur cells provide the highest proven energy to mass ratio of any available cell chemistry, offering three to five times the energy of a typical lithium-ion battery of the same weight. It has a theoretical specific energy of 2500 Wh/kg and theoretical energy density of 2800 Wh/l, making it a strong contender for ultra-high-endurance applications. Current practical cells can be made with performance about a quarter of this.

Unlike metal oxides, which tend to be heavy and expensive, sulfur as a cathode material is light and cheap. It is in fact one of the most abundant elements on earth, making it inexpensive and easy to obtain in large quantities.

Challenges

The major compromise is cycle life. Early Li-S batteries could withstand 50 to 100 charge cycles, which is too low for most mass-market applications. Reportedly the latest can achieve more than 1000. This is due to the 'polysulfide shuttle' effect, in which the sulfur cathode reacts with the electrolyte to form lithium polysulfides that move between the electrodes during charge and discharge, degrading both the sulfur cathode and lithium anode.

For the end user, the battery's short lifespan and the consequent need to replace it regularly may negate any cost savings passed on from the manufacturing process. Frequent disposal also creates additional logistical and environmental considerations.

In practice, the Li-S cell has yet to get anywhere near its theoretical energy density, topping out at around 300 Wh/l. Progress has been hampered by the material's low conductivity and the fact it expands by up to 80 per cent on cycling. This makes it unsuitable for situations in which space is constrained, such as small unmanned systems or handheld electronic devices. This limits its utility to large vehicles and static applications in which ample room is available.

Development

Preventing polysulfide shuttling is the key to extending the cycle life of the Li-S battery and making it commercially viable on a mass-market basis. Researchers have achieved incremental gains by adjusting the electrolyte system or applying protective coatings to the sulfur to retain dissolved material. But progress has been slow, leading some companies to abandon their research altogether. Sion Power, which developed and supplied the cells used on the *Zephyr* UAS, has since ceased its development of the technology to focus on lithium metal rechargeable cells, leaving UK-based Oxis Energy as the sole developer of near-commercial Li-S cells.

Oxis Energy's website provides a specification for a pre-commercial Li-S cell with a proven specific energy of 400 Wh/kg – almost a third higher than the best performing Li-ion cell – but with a comparatively low energy density of 300 Wh/l and a cycle life of 60 to 100 charges. Even its projections for future improvements are modest, predicting specific energy of up to 550 Wh/kg with energy density of 500 Wh/l, which still lags behind current lithium ion.

These factors mean it is likely to remain a high-value specialist item for niche applications in which run time and weight take precedence over total lifespan, size and cost. The Advanced Lithium Sulfur battery for Electric Vehicles (ALISE) project, conducted under the European Union's Horizon 2020 innovation programme, examined the potential market for lithium-sulfur cells¹⁷. It concluded that its higher specific energy and lower energy density than Li-ion makes it well suited to electric buses and aerospace, but unsuitable for small hybrid and plug-in hybrid electric vehicles.

In UK academia, fundamental studies to understand how the microstructure of the sulfur cathode changes with cycling has been undertaken by University College London. Fundamental research into the screening of electrolytes for Li-S batteries is ongoing at Southampton University.

Applications

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- Maritime Page 8

Pre-commercial lithium metal rechargeable cells

Commercial lithium metal batteries predate Li-ion by a couple of decades and are still widely used today in various formats, the most familiar being three-volt button cells. To date these have been available only as primary cells, as the ability to produce rechargeable models that are safe and durable has so far eluded developers. However, a number of companies are now marketing rechargeable cells on a pre-commercial prototype basis.

The cells currently in development are typically built using conventional Li-ion cathodes, but with an ultra-thin lithium metal anode instead of the usual graphite.

Advantages

At 3862 mAh/g, lithium metal has the highest specific capacity of any anode material. Lithium metal cells are claimed to be twice as effective as the best Li-ion models available today, with specific energy approaching 500 Wh/kg and energy density of up to 1200 Wh/l in some current prototypes. If these can be successfully commercialised, and the life and safety managed, they could launch the energy revolution needed to stop electric vehicles from being seen merely as an alternative to combustion engines and position them firmly as the buyer's first choice. Their high energy, combined with low weight and low volume, also make them an attractive prospect for portable electronic devices and unmanned aerial systems.

Challenges

Before rechargeable lithium metal cells can be commercialised, developers must solve problems caused by the build-up of lithium deposits known as dendrites on the anode. These grow like needles that can penetrate conventional separators, leading to short-circuits and causing fires. They also limit cycle life to a current maximum of around 375 charges – well short of the 1000-cycle target for electric vehicles.

Development

Several solutions are being explored to make lithium metal batteries safer and more durable through prevention of dendrite formation, including the addition of protective coatings to the lithium anode, chemical additives to liquid electrolytes, and incorporating ceramics into the separator.

Sion Power has adapted its Li-S technology to produce its *Licerion* brand lithium metal cell, comprising a conventional nickel-rich cathode and an 'ultrathin' lithium anode with protective coating, developed in collaboration with BASF, which has a \$50m equity investment in Sion. Initially targeting the unmanned aircraft system (UAS) market, the company claims it can achieve 496 Wh/kg specific energy and 929 Wh/l energy density in a 100 x 100 x 10 mm pouch cell.

Solid Energy, a spinoff from the Massachusetts Institute of Technology (MIT), is developing a lithium metal cell using an ultrathin lithium metal anode, nickel-rich cathode and ceramic-filled separator, which can provide 450 Wh/kg and 1200 Wh/l. Although conceived for the UAS, HALE and eVTOL markets, Solid Energy has announced plans to develop other product lines for consumer electronics and electric vehicles.

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Technologies: part two

Emerging high energy lithium-ion and related technologies

Nickel-rich cathodes

The main development trend in conventional lithium-ion cathodes has been a shift away from the established lithium cobalt oxide (LCO) chemistry. Cobalt is a costly, toxic element with a relatively low capacity, so developers are keen to explore alternatives. Nickel has been a popular substitute, being both less expensive and less toxic, but the direct analogue of LCO, lithium nickel oxide (LiNiO_2) is not sufficiently stable. Developers have sought to stabilise nickel-based cathodes by combining nickel with cobalt alongside other metals such as aluminium and manganese.

Advantages

The low cost and high capacity of nickel relative to cobalt makes it an attractive prospect for mass-market applications. Nickel cobalt manganese variants have proven effective in mobile phones and other consumer electronic devices, while nickel cobalt aluminium (NCA) is employed in commercial electric vehicle cells manufactured by Panasonic and Tesla.

Challenges

The major trade-off is between capacity and stability. Higher nickel content offers more energy, but reduced cycle life.

Although researchers have put a great deal of effort into optimising capacity and cycle life of nickel-rich cathodes, the approach by itself can provide only incremental improvements in specific energy and energy density, rather than the step-change needed to make them commercially viable.

Development

Developers have been busy experimenting with ratios of metal content, making small incremental changes to the chemical composition of cells and testing them. Present-day fully commercial cells are thought to employ nickel, manganese and cobalt at ratios of 1:1:1 (NMC111) and 5:2:3 (NMC523), offering capacities of around 155 and 165 mAh/g respectively. Prototypes using NMC622 and NMC811 ratios are believed to be close to market, potentially delivering up to 175 and 200 mAh/g.

The alternative to tweaking chemistries is to radically redesign the physical structures of batteries, increasing the percentage of active material inside from a typical 30 per cent to perhaps 50 per cent. LG has reengineered its batteries to achieve 20% more energy in the same phone case. However, the Samsung Galaxy Note 7 serves as a cautionary tale against attempting to pack too much into too small a space.

Another way of increasing capacity of cells utilising NMC materials is to increase the operating voltage beyond 4.3 V. A group of South Korean researchers has recently demonstrated that NMC622 cycled to 4.5 V exhibits greater stability and capacity after 100 cycles than NMC811 at 4.3 V.

Many other potential developments are in the pipeline and Faraday Institution research through its next generation cathode projects will be investigating some of these. Of particular note is the focus on engineered particles and single crystal structures for the transition metal oxide chemistries and the inclusion of other elements such as sulfur and halides.

Applications

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Vanadium-based cathodes

There are other families of high-capacity intercalation materials that would be compatible with existing lithium-ion configurations, as well as having the potential to be used for future solid-state and lithium-metal cells. Vanadium-based materials have received considerable interest, with electroactive lithium vanadyl phosphate (LiVOPO_4) having shown particular promise.

Advantages

Like nickel-rich cathodes, those employing vanadium may provide higher capacity at a reduced material cost.

Challenges

LiVOPO_4 and similar materials tend to exhibit low conductivity and poor cycle life. They are at lower technology readiness levels, so have a long way to go before they are ready for commercialisation.

Development

Researchers from Germany and Estonia have reported intercalation of up to 420 mAh/g for $\text{Li}_2\text{VO}_2\text{F}$ in half cells

with lithium. The cycle life reported in these experiments was modest, but the early results show promise.

Conductivity and cycle life issues were previously successfully overcome for LiFePO_4 as a cathode material, using a combination of carbon-coating and nanosizing, to the extent that its use is now widespread in large-scale applications. A similar approach to improving performance has been considered for other materials, including LiVOPO_4 . Collaboration between researchers at Binghamton University in the US and Professor Clare Grey's research group at Cambridge University reported reversible capacity of 250 mAh/g over 70 cycles for a ϵ - LiVOPO_4 material.

Applications

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High-voltage cathodes

Increasing a cell's operating voltage by adopting new cathode materials, such as lithium-nickel-manganese oxide (LNMO) and lithium cobalt phosphate or other transition metals such as manganese or vanadium, may increase specific energy and energy density by improving the battery's efficiency.

Advantages

Large battery packs, such as those used in today's electric vehicles, are composed of multiple cells in a series. The connections that join these cells are a source of resistance, causing incremental reductions in voltage as electrons pass through them. It may be possible to counter this effect by increasing the operating voltage of each cell, meaning fewer cells and associated interconnections are needed. This would reduce overall resistance and increase the battery's efficiency. This solution hypothetically decreases the mass and volume of the battery pack without reducing its energy.

Challenges

The main factor holding back the development of high-voltage cathodes is the absence of an equally high-voltage electrolyte. Existing organic solvent-based electrolytes decompose and become unstable at higher voltages, making them unusable – but a suitable synthetic alternative may not yet have been found. Efforts to date have produced mixed results, with most suffering from very poor cycle life. Although some claim to have solved this, evidence has been difficult to identify.

Development

To focus on novel cathode materials at this stage of development would be premature. More research is needed to identify an electrolyte that can handle the voltages produced by the cathode. Only once the electrolyte material is defined can the cathode material be developed.

Thankfully, such research is currently underway. Academia and small to medium-sized enterprises (SME) are

working together on potential remedies, including inorganic solid-state electrolytes and others based on ionic liquids.

Researchers at the University of Maryland, led by Chunsheng Wang, have announced promising results for a battery employing a LiCoMnO_4 cathode with graphite and lithium metal anodes, which uses a specially designed electrolyte stable to 5.5V. Using this electrolyte, LiCoMnO_4 cells with lithium anodes can provide 720 Wh/kg for 1000 cycles at 5.3 V, while those with graphite anode produce 480 Wh/kg for 100 cycles at 5.2 V.

In the UK, researchers at the University of Sheffield have produced a LiCoMnO_4 cell which, when cycled between 3.0 and 5.3 V, exhibits higher capacity (up to 110 mAh/g), higher coulombic efficiency and better capacity retention over the 20 cycles reported than cells using unmodified electrolyte. The researchers highlighted the need for further optimisation of electrolyte composition to improve cycle life.

Applications

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Silicon anodes

Silicon is denser than graphite and possesses a much higher theoretical capacity, making it an attractive prospect as an anode material. Silicon and silicon-oxide materials are already used alongside graphite in composite anodes for some commercial cells, but these typically contain no more than around five per cent silicon by weight. Some researchers are exploring ways to increase the silicon content of composite anodes, while others are trying to produce anodes formed entirely out of the material. Although our focus here is on energy density, Silicon added to the anode also allows the use of “fluffy” carbon material which has a higher power capability at the anode and hence more rapid charging.

Advantages

The theoretical capacity of silicon, at 3600 mAh/g, is almost ten times that of graphite. This allows for much thinner electrodes, ultimately resulting in a smaller cell that contains a lot more energy. Manufacturers of compact consumer electronics are likely to watch this technology's progress very closely. One Californian developer, Enovix, claims that its pure silicon anode provides an 80% increase in energy density for wearable devices and 30% for smartphones. The company does not provide metrics for specific energy, but in December 2018 another Californian company, Amprius, reported that its silicon anode lithium-ion cells had been successfully demonstrated in Airbus's *Zephyr S* pseudo-satellite. This technology delivers specific energy of 435 Wh/kg, exceeding that of *Zephyr's* previous Li-S cells by around 100 Wh/kg.

Challenges

Silicon 'swells' as it takes on lithium ions, increasing in size by up to 320 per cent. Repeated expansion and contraction as the cell is charged and discharged causes the anode to fracture and degrade, leading to a rapid decline in its capacity.

Development

Of the companies seeking to increase the silicon content of composite anodes, the UK's Nexeon is perhaps the most notable. The company has been developing silicon anode materials since 2006 and currently offers two different types of silicon material. The first, NSP-1, is a silicon composite powder for use in conventional graphite anodes to improve capacity. It is said to give typical anode capacity of 400 to 450 mAh/g. The second, NSP-2, is a 'silicon-based material' designed to mitigate expansion through a combination of engineered porosity at a particle level and optimised anode design. According to Nexeon, the material provides a 'significant' increase in anode capacity, although metrics have not yet been released. Further development of Nexeon's silicon anodes continues, partly funded by the Faraday Battery Challenge project SPICE (Silicon Product Improvement through Coating Enhancement). The project team, which also includes Phoenix Scientific Industries (PSI), AGM Batteries, and the Department of Materials at Oxford University, will develop enhanced carbon surface coatings for the silicon to avoid the need for higher cost electrolyte additives.

In the world of pure silicon anodes, several developers are researching innovative structures that are capable of taking on more lithium without fracturing. Amprius has developed a porous, amorphous nanowire structure that it claims reduces swelling to less than 30 per cent and eases stresses associated with expansion and contraction. The anode can reportedly be used over 'hundreds' of cycles, closing in on the performance of graphite anodes. Although Amprius's own cell technology is not yet fully commercial, the company also provides its nanowire silicon materials to be used as additives to graphite anodes in other manufacturers' cells.

Dutch Company Leyden Jar uses a technique borrowed from the semiconductor industry called plasma-enhanced chemical vapour deposition (PECVD) to deposit silicon onto a copper column. These porous anodes are produced in a single manufacturing step and can reportedly be used to produce cells of up to 1200 Wh/l or 450 Wh/kg with a cycle life of 570 cycles. If true, this would allow it to compete with Li-ion. Leyden Jar aims to demonstrate semi-commercial production in 2019.

Both Amprius and Leyden Jar pair structured anodes with conventionally produced intercalation cathodes in a standard Li-ion cell format, but Evonix has developed a whole cell architecture of its own, using silicon wafers a millimetre thick stacked with the cathode and separator materials to form a three-dimensional structure. The company claims its format is more volume-efficient than conventional lithium-ion products. A prototype cell designed to fit in a smart watch is said to reach 695 Wh/l, compared to 460 Wh/l for the conventional lithium-ion cell.

Applications

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Tin-based anodes

Like silicon, tin can reversibly react to form alloys with lithium. While tin's gravimetric capacity is lower than that of silicon, its volumetric capacity is similar.

The incorporation of tin-based anode materials into commercial cells predates silicon, with Sony's Nexelion 14430 lithium-ion cell, introduced in 2005. These cells employed a composite anode consisting of approximately half

graphite and half 1:1 tin-cobalt alloy.

In 2011, Sony released a second-generation Nexelion cell in the common 18650 format, which achieved 723 Wh/l, and 226 Wh/kg. At that time, this was around 30 per cent higher than equivalent cells based on graphite alone.

Advantages

Tin anodes have high gravimetric and volumetric capacities. The theoretical capacity of pure tin is 993 mAh/g, while tin oxide (SnO_2) has a theoretical capacity of 782 mAh/g. Tin is also environmentally benign, inexpensive and safe.

Challenges

Like silicon, tin exhibits large volume changes on cycling (300 per cent), leading to similar electrode degradation and capacity fade issues.

Development

Various strategies have been employed to minimise or accommodate the large volume change on cycling:

- Composites with carbon-based materials to accommodate strain during cycling, such as carbon nanotubes and microporous carbon
- Intermetallic alloys with metals such as cobalt, copper, lanthanum, nickel, molybdenum, iron, manganese, silver, vanadium or titanium
- Tin compounds – oxides, fluorides, sulfides, nitrides

These materials have been employed in a number of tailored structures, such as core-shell, 2-D layered structures, nanowires, nanotubes and anchored structures.

In the research paper “Oxidized Co-Sn nanoparticles as long-lasting anode materials for lithium-ion batteries”, published in the journal *Nanoscale*, the authors report a CoSn_2O_x anode with a high capacity of 525 mAh/g after 1500 cycles – 92 per cent of the starting capacity.

Researchers at the University of Southampton have reported a Sn_3N_4 anode for potential use in Li-ion and Na-ion, but the practical specific capacities reported at 50 cycles are not particularly high, at 270 mAh/g for sodium and 370 mAh/g for lithium.

A group of researchers including Dan Brett and Jawwad Darr of University College London has studied the effect of a range of nine different metal ion dopants on the performance of SnO_2 anodes. Of the dopants tested, only the sample with nine per cent cobalt was shown to enhance performance over the non-doped material, giving a capacity of 953 mAh/g and coulombic efficiency of 79.4 per cent, compared to 812 mAh/g and 62.5 per cent for un-doped SnO_2 . The researchers concluded that doping may not be beneficial for increasing energy density if the electrodes were to be used in full cells in the future.

Applications

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Conversion electrodes

Unlike lithium-ion batteries based on intercalation, in which lithium ions shuttle between a lithium-metal oxide cathode and a graphite anode, conversion batteries produce current via a reversible chemical reaction.

This mechanism is not uncommon in other battery systems; both lead acid and sodium sulfur are examples of large-scale commercial battery systems based on conversion chemistry as are currently commercial lithium-sulfur and metal-air cells.

Advantages

Various materials have been investigated for use as conversion anodes, such as metal oxides, phosphides, sulfides and nitrides, all of which offer higher theoretical specific capacities than graphite, ranging from 500 to 1800 mAh/g. This would enable production of a battery with a greater capacity than existing graphite-based models, but without the disadvantages associated with silicon.

A number of materials have also been studied as potential conversion cathodes, the attraction being a much higher specific capacity than the conventional lithium-ion cathode.

Examples are:

- Fluorides: TiF_3 , VF_3 , CrF_3 , FeF_3 , NiF_2 , CoF_2 , CuF_2
- Chalcogenides: Li_2S , Li_2Se , Li_2Te

As well as a high specific capacity, CuF_2 has a theoretical operating voltage which is close to that of intercalation cathodes and so offers the clearest potential benefit as an alternative cathode material. It has been projected that an idealised CuF_2 based cell could achieve 1896 Wh/l and 983 Wh/kg with a lithium anode, and 980 Wh/l and 420 Wh/kg even with a conventional graphite anode.

Challenges

Conversion systems have several drawbacks.

Because energy must be expended in the reaction, there is usually significant hysteresis between charge and discharge voltage, which has been attributed to differing electrochemical reaction paths for the charge and discharge processes. This results in reduced energy efficiency (often less than 80 per cent) compared to lithium-ion (typically greater than 99 per cent under ideal charging conditions) and heat generation, which may be difficult to manage.

The conversion reactions also tend to result in major structural reorganisation, potentially leading to loss of electrical contact and degradation of the electrode, and in turn limiting cycle life.

Conversion anodes typically exhibit much greater first-cycle irreversibility than conventional anodes, which must be compensated for by starting with a larger excess of the cathode material for example, potentially negating some

of the capacity increase.

With the exception of CuF_2 , many conversion cathodes exhibit much lower electrode potentials than existing lithium ion cathode materials, so would not be a direct replacement for existing lithium-ion systems.

These types of materials also typically react with conventional electrolytes, so new electrolyte systems must be developed.

Development

The range of possible conversion anode and cathode materials is very wide, but all are at a low technology readiness level. At this early stage it is difficult to predict which are most likely to succeed, and such work is probably best suited at present to academia.

Academics in China have reported a nanocrystalline manganese(II) fluoride anode material with a reversible capability of 481.9 mAh/g at 0.1 C for the first cycle and stable discharge capability of 530.5 mAh/g and 359.2 mAh/g at 0.1 C and 1 C for 250 cycles respectively .

The article "High energy-density and reversibility of iron fluoride cathode enabled via an intercalation extrusion reaction," published in *Nature Communications*, reports a system that achieved good reversibility over 1000 cycles and 420 mAh/g capacity using iron fluoride nanorods doped with cobalt and oxygen. Not only does this system achieve an energy density of around 1000 Wh/kg with a decay rate of only 0.03% per cycle, but the authors believe the co-substitution strategy could be extended to improve the performance of other high energy conversion cathodes.

Iron fluoride (FeF_3) shows promise as a conversion-intercalation cathode material for lithium-ion cells, as it has a very high theoretical specific capacity of 712 mAh/g, but unfortunately exhibits poor electrochemical reversibility.

In the UK, Professor Clare Grey has previously collaborated with researchers at Brookhaven National Laboratory, State University of New York at Binghamton, Rutgers University, and Stony Brook University on binary fluoride (FeF_2 and CuF_2) conversion cathodes.

Applications

Due to the range of different properties, it is too early to specify applications.

Technologies: part three

Lithium-metal cells

Lithium-oxygen

Metal-air cells, which use oxygen from the air as the active cathode material and a reactive metal as the anode, have been something of a holy grail in battery research circles since the 1970s. In a lithium-oxygen (also known as lithium-air) cell, current is generated by the oxidation of lithium at the anode and reduction of oxygen at the cathode. Recharging reverses the reaction, returning the oxygen to the atmosphere. In theory, lithium-oxygen provides the highest possible specific energy of any battery, but much research is needed before the theoretical possibilities can translate into reality.

Advantages

Lithium-oxygen cells have the potential to provide up to five times the energy density of current Li-ion technology. Using just 60 kg of these batteries – roughly the same mass as a full petrol tank – a 2000 kg electric vehicle could travel 500 kilometres on a single charge.

The other obvious advantage of using air as a cathode material is that it is free and abundant, although it is too early to know for certain whether the resulting cost savings will compensate for other expenses incurred during the manufacturing process.

Challenges

Most prototypes are tested using pure oxygen, but for a lithium-oxygen cell to be commercially viable it would need to operate without an air tank using the normal air around it. The air that we breathe contains many contaminants, such as moisture and carbon dioxide, which can degrade the battery's component parts, leading to poor reversibility and cycle life.

The technology is currently inefficient due to an imbalance between the battery's input voltage when charging and output voltage when discharging, which causes up to 30 per cent of electrical energy to be wasted as heat during each cycle.

Although its energy density is very high, the rate at which a lithium-oxygen battery discharges that energy is lower than contemporary Li-ion batteries, meaning power is limited. Using a lithium-oxygen battery, an electric vehicle could drive for a long time on a single charge, but at the cost of speed, acceleration and charging performance.

Lastly, the reduction of oxygen requires a reaction surface and catalyst. The materials currently in the frame to fulfil this role – such as manganese, cobalt, ruthenium, platinum, and silver – tend to be expensive, and so work is still needed to identify cost-effective, stable materials that are up to the task.

Development

A recent paper from researchers at Linda Nazar's group at The University of Waterloo in Canada demonstrated a novel inorganic electrolyte Li-O₂ cell that operates at 150°C. By operating at elevated temperature, the cell was shown to reversibly cycle at close to 100 per cent efficiency for 150 cycles with pure oxygen, delivering a capacity of 11 mAh/cm². Although such a high operating temperature would not lend itself to consumer electronics, if developed further it could be suitable for electric vehicles and large scale energy storage.

UK academic researchers continue to play a major role in the development of lithium-air batteries with many leading battery scientists investigating potential solutions.

Despite promising progress, commercialisation of lithium-oxygen technology is thought to be at least five to 10 years away. The first products are likely to be very high energy primary cells for niche applications, as rechargeability remains the biggest hurdle for a cell operating on normal air.

Applications

- Electric vehicles Page 3
- Large-scale storage Page 9

Technologies: part four

Solid-state batteries

Solid-state batteries

As the name suggests, solid-state batteries are distinguishable by their lack of liquid electrolyte. They instead rely on inorganic solid-state electrolytes, which generally fall into one of three classes: ceramics; glasses; or sulfides. Earlier attempts to use organic polymers failed to bear fruit, largely because the materials had to be heated to between 60 and 80 degrees Celsius. The newer synthetic materials can function at room temperature, prompting a resurgence of interest that has led solid-state cells to be considered among the most promising future battery technologies. In the past, manufacturing techniques have generally limited their potential uses to micro-scale devices operating at low power, but a great deal of research is now being conducted in an effort to scale up the technology. This research is strongly supported by major motor manufacturers such as Ford, General Motors, Toyota, BMW, Honda and Volkswagen.

Advantages

The potential risk of contemporary Li-ion batteries to ignite when damaged or faulty remains a driving force behind the search for an alternative. Solid-state batteries, by dispensing with flammable liquid electrolytes, could go a long way to allaying these concerns.

Solid-state electrolytes are generally compatible with existing cathode materials and should also be capable of tolerating future, higher-voltage cathodes. They have been touted as one of the most promising options for enabling the use of lithium metal anodes, opening the door for higher energy density and specific energy.

The solid electrolytes possess lower conductivity than liquids, but can be made thinner to compensate – which may actually prove an advantage, as a greater proportion of the cell can be made up of active material, increasing energy density.

Finally, it may be possible to print solid-state batteries using additive manufacturing techniques, which could significantly reduce production costs and turnaround times.

Challenges

Although the use of solid-state electrolytes is widely promoted as a means of enabling the use of lithium metal anodes by prohibiting dendrite penetration, recent research has cast doubt on that assertion. In response to adverse findings by other researchers, a team from the University of Maryland and Oak Ridge National Laboratory in the US examined dendrite formation and observed that it was actually easier for them to form in high-conductivity solid electrolytes than in conventional liquids. They concluded that the cause of lithium growth is independent of the density of the solid electrolyte or its structural integrity, but is in fact directly linked to the high conductivity. The findings of this work contrast strongly with the general direction of solid-state electrolyte research, which has been to improve electrical performance by increasing the conductivity of the solid electrolyte.

Development

Developers of solid-state battery technology include US company SolidPower, a spinoff from the University of Colorado at Boulder. According to its website its cells use lithium metal anodes, a "high ionic conductivity inorganic solid separator" and a high capacity cathode. The company is reported to have made laboratory scale cells at 400 to 500 Wh/kg, capable of up to 500 charge cycles and projects the following metrics at an unspecified cell scale:

- Specific energy: 320-700 Wh/kg
- Energy density: 700-1100 Wh/l
- Power density: >1000 Wh/kg
- Cycle life : >1000 cycles
- Shelf life: >10 years

Another US developer, Ionic Materials, has developed a solid-state polymer electrolyte which exhibits high conductivity at room temperature. Rather than develop its own cells, Ionic sees its novel electrolyte as an enabler across a variety of different chemistries, including lithium-sulfur and lithium-metal cells with conventional cathodes. To accelerate commercialisation of its technology, it has teamed with A123 Systems to develop electric vehicle-sized NMC/graphite lithium-ion cells, which it aims to begin manufacturing on a large scale as soon as 2022.

In the UK, Ilika is developing lithium-ion technology using an inorganic solid-state electrolyte. Ilika's current products are micro-batteries designed for sensors, Internet of Things (IoT) devices and other small-scale applications. Starting in around 2020, the company plans to scale up its technology to electric vehicles and stationary power. It claims the new range could reach 1000 Wh/kg with a 10-year operating life, but has not yet given an indication as to how this scale-up might be achieved.

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Technologies: part five

Beyond lithium

Multivalent ion chemistries

Lithium is a monovalent metal, meaning it is capable of transferring just one electron per atom of lithium during the cell reaction. Multivalent metals are those capable of transferring more than one electron per atom. Using these metals in batteries could increase their energy, so there is interest in applying them to cells that use similar chemistries to lithium-ion. The metal that has received the most attention is magnesium, which can transfer two electrons – but others include calcium and zinc, each able to transfer two electrons, and aluminium, which can transfer three.

Advantages

Magnesium as an anode material has a high volumetric capacity, offering 3833 mAh/cm³ compared to the 2046 mAh/cm³ provided by lithium. It is safe to use in its metallic form and does not form dendrites, which removes many of the practical difficulties associated with lithium-based cells. It is also more abundant and less expensive than lithium, making it an attractive prospect for certain mass-market applications.

Challenges

The principle issue facing developers is finding a suitable cathode material to match.

In general, magnesium intercalation is very slow at room temperature, resulting in significant voltage hysteresis between charge and discharge. Even the most successful intercalation cathode demonstrated to date at room temperature exhibits low capacity, at 120 mAh/g, and low voltage, at 1.2 V. Others exhibit higher voltage and therefore a higher theoretical capacity of up to 400 Wh/kg, but show very poor intercalation ability at room temperature.

One way of overcoming this may be to couple a magnesium metal anode with a mature lithium-ion battery type cathode, but this arrangement requires a significant excess of electrolyte, which negatively impacts energy density and specific energy.

Development

Rechargeable magnesium batteries have only been seriously studied for around a decade, so are in their infancy in comparison to Li-ion systems. There are potential long-term benefits, but it is difficult to assess which is the most promising of the large number of systems studied.

In the UK, research into multivalent chemistries is being performed by several research groups. The universities of Cambridge and Sheffield are investigating magnesium-ion, while Southampton University is exploring aluminium-ion.

Elsewhere, the 2018 article, "A critical review of cathodes for rechargeable Mg batteries," published in the journal, *Chemical Society Reviews*, reports on the range of potential cathode materials, and on the large number of intercalation, conversion and redox cathodes.

All multivalent chemistries are at a comparable stage of development and present similar issues. It would appear that none of the technologies studied to date are likely to yield a practical high energy system in the near future, although low-cost, low-energy versions may reach commercialisation in the interim.

Applications

- Large-scale energy storage

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Aluminium-air

Following the same basic concept as lithium-air, the aluminium-air variant has garnered much interest as a lower-cost alternative to high-energy battery technology's "holy grail." Electricity is generated as the aluminium anode reacts with oxygen in the air, which can either be introduced passively via a membrane or similar component, or delivered actively using pumps or fans.

The aluminium is consumed by the reaction and so currently these batteries cannot be recharged in the conventional electrochemical sense. The current early variants are designed to be mechanically recharged by removing waste discharge products, installing new aluminium anodes and replacing the electrolyte.

Advantages

Such systems are proposed for a variety of applications, including electric vehicles, where they are thought to offer up to eight times the driving range of a lithium-ion battery. The aluminium anode is claimed to enable a practical specific energy of 8000 Wh/kg, and a car powered by the technology could conceivably travel over 1000km on a single charge. Although the battery is not electrochemically rechargeable, the aluminium waste products are readily recyclable, minimising the environmental impact of disposal associated with many other battery types.

Challenges

The flow of current can be inhibited by an oxide layer that forms on the aluminium surface, limiting the battery's performance. To counter this effect, the cell must either employ specialised aluminium alloys, which can be expensive, or rely on electrolytes that are corrosive and typically caustic, making safe handling and environmentally-friendly disposal a challenge.

The need to access air probably precludes routine use in consumer electronics, which are increasingly sealed to protect against dust and water ingress. Air delivery is not an issue for vehicles, for which fans and air pumps have long been features, although the inability to electrically recharge may present a problem for domestic car owners. The process of mechanically charging the battery is cumbersome and requires specialist equipment, meaning the technology is best suited to organisations with fleets of vehicles, where the recharging infrastructure can be centralised. The cars themselves may have to be redesigned from the ground up to accommodate the batteries, which are unlikely to be compatible with existing vehicle architectures.

Development

Israeli company Phinergy is the source of the "1000-mile" claim. With the backing of Alcoa, the world's largest aluminium producer, it demonstrated its aluminium-air concept car at the Circuit Gilles-Villeneuve in Montreal in 2014, subsequently raising \$50m in investment.

Phinergy has also produced a containerised 5.8 kWh system for marine energy storage.

In the UK, aluminium-air technology is being developed by Métaelectrique, which claims up to 1300 Wh/kg for a vehicle-sized system. It is also developing a specialised military battery product which is probably nearer commercialisation. Métaelectrique's key intellectual property is its proprietary electrolyte, which is non-corrosive but still allows the use of inexpensive aluminium grades.

Applications

- Electric vehicles Page 3
- Large-scale energy storage Page 9

Conclusions

What is the best high-energy battery technology available today?

Lithium-ion is the incumbent market leader, favoured because of its high energy density, high specific energy, and versatility that makes it suitable for applications from consumer electronics to electric vehicles. The European Commission expects annual demand for car batteries and energy storage to increase by ten times between 2018 and 2028, and predicts a further surge before 2030 as mass manufacturing halves the cost of lithium-ion cells through economies of scale and streamlined production processes. Lithium-ion's past track record, and continuing ability to satisfy some of today's most demanding energy challenges, means it will remain the battery of choice for at least the next ten years.

However, lithium-ion is not perfect. Safety issues, while still relatively rare, have led to a number of very high-profile incidents in which the batteries in mobile devices and electric vehicles have caught fire, putting their users in danger and causing financial and reputational damage to the manufacturers. Most companies would be keen to reduce this risk by embracing safer alternatives, if researchers are able to prove that they are high performing and cost effective.

We are also witnessing a slowdown in advancement regarding conventional lithium-ion batteries, in which improvements are becoming ever more incremental as they approach the physical performance limits. Progress may not come to a complete halt, but it is not inconceivable that other technologies will begin to overtake it within the next decade as research into alternative chemistries gains momentum.

What is the most promising emerging technology?

In the near-term, variants on existing lithium-ion formats will produce the biggest gains in energy density and specific energy. The use of higher energy cathode materials such as lithium nickel cobalt aluminium oxide (NCA) and lithium nickel manganese cobalt oxide (NMC) has led to increased capacity in commercial cells, but in the near to medium-term augmenting or replacing graphite as the standard anode material is likely to offer more significant improvements. Silicon is becoming increasingly common in small quantities in some commercial cells and some scientists have high hopes for pure silicon and tin-based anodes, which could deliver big increases in energy density if efforts to mitigate degradation caused by swelling prove successful.

Developing in parallel with silicon and tin anodes, lithium metal offers the most scope for increased capacity. With existing prototypes reaching 500 Wh/kg specific energy and 1200 Wh/l energy density, lithium metal could prove twice as effective as lithium-ion; but only if developers can demonstrate sufficient cycle life and solve the safety problems caused by dendrite formation.

In the long term, developers will continue their quest for the holy grail of high-energy battery technology. Metal-air cells are potentially five times more energy dense than today's lithium-ion technology and use air as a cathode material, which is abundant, free to obtain, and environmentally friendly. However, there is still a long way to go before the technology's efficiency, power, durability, and affordability reach levels that will make it a realistic commercial prospect.

Looking even further ahead, battery users could benefit from research that produces lower-cost alternatives to lithium. In addition to the well-publicised safety issues, international trade wars and political instability in the countries in which lithium is mined means continuity of the supply chain may not always be guaranteed and prices may be prone to unpredictable fluctuations. Magnesium, calcium, zinc and aluminium are all being investigated, but have yet to yield a practical high-energy system.

The final word

While there are several possible contenders to lithium-ion's throne, there is no single silver bullet that will solve all challenges for all markets. Any organisation seeking to electrify its products and services, or increase the energy of its existing offerings, must understand the unique properties of each battery type and choose the solution that is the best fit for its specific purpose. That decision will inevitably involve an acceptance of compromises, as maximising a system's energy density or specific energy may come at the cost of power, cycle life, safety or affordability. Developers must consider the extent to which energy adds value, and decide what they are willing to sacrifice to maximise it.

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Appendix 1 - Estimated value

Sector	Current or recent market value (2014-18) (US\$)	Prediction date range	Market value in prediction (US\$)	CAGR (%)
Portable consumer electronics	1,172 billion	2018-2024	1,787 billion	6.0
Portable consumer electronics batteries (0-3000 mAH vs. NMC)	N/A	2018-2026	29.28 billion	N/A
	N/A	2018-2026	39.01 billion	N/A
Electric vehicles	118.86 billion	2018-2025	567.3 billion	22.3
Electric vehicle batteries	23 billion	2017-2025	84 billion	17.2
Civil aviation	N/A	2019-2024	224.5 million	N/A
E-VTOL	N/A	2019-2027	315.2 million	12.6
High altitude platforms	2.3 billion	2015-2023	4.77 billion	8.7
Unmanned systems (UAV vs. USV)	18.14 billion	2018-2025	52.3 billion	14.15
	534 million	2018-2023	1.02 billion	13.8

Appendix 2 - Emerging technology summary

Time to commercialisation	Battery type	Development Status	Nominal cell voltage/V	Specific Energy/Wh/kg	Energy Density/Wh/l	Cycle life	Notes
Available now	Lithium-ion with graphite/silicon anodes and NCA or NCM cathodes	State-of-the-art commercial cells	3.7	240 - 270	600-650	1000 -2000	e.g. Tesla 21700 cylindrical cells (NCA) NCM 532 cathode cells pouch or cylindrical formats
		Commercial prototype cells	3.7	Up to ~300	Up to ~700	>1000	NCM 622/811 cathodes
Ready for commercialisation	Lithium-ion with pure silicon anodes and nickel-rich cathodes	Commercial prototype cells	Not specified	465	Not specified	Not specified	Ampricus Si-nanowire anode cells- as demonstrated in Airbus Zephyr-S
			Not specified	Up to 450 (projected)	Up to 1200 (projected)	>570	Leyden Jar PECVD anode
	Lithium metal anode- NCM cathode	Commercial prototype cells	3.82	426 - 496	807-929	>350	Sion Power "Licerion" 6 Ah and 20 Ah cell variants
			3.8	450	838 for prototype cell, "up to" 1200 projected	>120	Solid Energy "Hermes" 3 Ah cell prototype (+projected future cell performance for larger cells)
	Lithium-sulfur	Commercial prototype cells	2.1	400 (up to 550 projected for future cells)	300 (up to 500 projected for future cells)	60-100 (100% depth of discharge) ~200 (60% depth of discharge)	Oxis Energy 14.7 Ah cell
Up to 5 years	Solid state electrolyte cells with lithium metal anode and nickel-rich intercalation cathode	Commercial prototype or pre-prototype cells	~3.8 V	400-700 (up to 1000 projected for future)	700-1100	>1000	Current and near-future metrics based on SolidPower cell characteristics. Both Ilika (UK) and Innolith (Switzerland) project 1000 Wh/kg achievable for EV-scale system based on lithium-metal anode based system. No information is provided by either developer on how this would be practically achieved
	Aluminium-air	Commercial prototype or pre-prototype cells	~1.5 - 2 V (dependant on air electrode characteristics and system design)	Up to 1300 claimed	Not specified	Not electrically rechargeable - "mechanically rechargeable" by anode and electrolyte replacement	Developers include Métaelectrique (UK), Phinergy (Israel)

continued on next page

Appendix 2 - Emerging technology summary (continued)

Time to commercialisation	Battery type	Development Status	Nominal cell voltage/V	Specific Energy/ Wh/kg	Energy Density/ Wh/l	Cycle life	Notes
Over 5 years	High voltage LiCoMnO ₄ cathode with lithium metal or graphite anodes	Small scale Laboratory prototype cells	4.7-5.3 (vs Li) 4.6-5.2 (vs graphite)	720 (vs Li) 480 (vs graphite)	Not specified	1000 vs lithium in test cells, lithium-ion cells with graphite exhibited only 100 cycles	Wang Chunsheng – University of Maryland Li-metal cells might achieve ~1300-1400 Wh/l if exhibit similar relationship between mass and volume as comparable cells
	Conversion cathode (Fe _{0.9} Co _{0.1} OF)	Small scale laboratory prototype cells	~2 V (average voltage for sloping discharge profile)	1000 in "half-cell" tests vs Li	Not specified	1000 cycles in half-cell tests	Most promising example data for Fe _{0.9} Co _{0.1} OF nanorods given. Such systems suffer from large voltage hysteresis and typically exhibit poor cycle life in full cells
Up to 10 years	Lithium-oxygen / lithium-air	Low TRL - laboratory research	~2.9	Up to 3500 (theoretical) Up to 1000 projected for a practical system	Dependent on system	100s to 1000s (depending on depth of discharge) in oxygen.	Good cycle life has only been successfully demonstrated using pure oxygen. Potential first commercialisation as high capacity primary.
	Conversion anodes e.g. transition metal oxides, phosphides, sulfides and nitrides	Low TRL - laboratory research	Dependent on system	Dependent on system	Dependent on system	Poor cycle life	High theoretical capacity (~500 to 1800 mAh/g), but suffer from large voltage hysteresis, poor cycle life (as a result of deterioration because of structural reorganisation).
	Multivalent intercalation cell chemistries based on aluminium, calcium, magnesium or zinc	Low TRL - laboratory research	Dependent on system	Dependent on system	Dependent on system	Dependent on system	Systems tested to date exhibit poor performance vs the theoretically high capacity predicted based on the multi-electron reactions for multivalent systems. If projected high energy performance remains unachievable these systems may still offer cost benefits for large-scale energy storage application.

Notes on status definitions used in the table:

Commercial cells – full-commercial scale manufacturing and supply.

Commercial prototype cells – cells available to selected customers for evaluation or in-house prototype versions of next-generation products, which are amendable to production scale-up in the near term.

Commercial pre-prototype – cells demonstrated by commercial developer in-house, which also have been validated by independent testing. Potential for scale-up to commercialisation within 5 years.

Small scale laboratory prototype cells – demonstrations of small-scale cells (typically in academic/national Research laboratory environment. Projection of representative cell specific energy and/or energy density characteristics. Possible commercial exploitation in 5+ years.

Low-TRL laboratory research – individual anodes, cathodes or other components demonstrated at test-cell level. Often results reported are for so-called "half-cell" tests vs lithium. In such cases, the lithium electrode is usually in large excess, which can result in unrealistic prediction of cycle life and other metrics. There may be limited or no projection of full cell characteristics. Further R&D required to exploit on 5-10 year timescale at best.

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