

History, Evolution, and Future Status of Energy Storage

This paper discusses the important aspects of energy storage including emerging battery technologies and the importance of storage systems in key application areas including electronic devices, transportation, and the utility grid.

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ABSTRACT | Advanced energy storage has been a key enabling technology for the portable electronics explosion. The lithium and Ni-MeH battery technologies are less than 40 years old and have taken over the electronics industry and are on the same track for the transportation industry and the utility grid. In this review, energy storage from the gigawatt pumped hydro systems to the smallest watt-hour battery are discussed, and the future directions predicted. If renewable energy, or even lower cost energy, is to become prevalent energy storage is a critical component in reducing peak power demands and the intermittent nature of solar and wind power. An electric economy will demand more electrification of the transportation sector and it is likely that all vehicles sold by the end of this decade will have some level of hybridization. Energy storage capabilities in conjunction with the smart grid are expected to see a massive leap forward over the next 25 years.

KEYWORDS | Battery; electric economy; energy storage; pumped hydro

I. THE NEED FOR ENERGY STORAGE

Why is there a need to store energy and in particular electrical energy? Energy storage is a critical component of manufacturing, of the service industry, of the future renewable energy industry, and of all the portable electronics with which we have become obsessed. Without modern energy storage, using lithium-ion (Li-ion) bat-

teries, the decade of the smartphone, iPad, and iPod would not have progressed like it did [1]. Besides entertainment, energy storage plays a critical role in high-tech manufacturing where it is essential to have an uninterruptable power source of constant frequency. It is reported that some \$80 billion is lost by U.S. industry [2] each year because of mainly short power interruptions. To ameliorate this, high-tech high-cost industry such as chip fabs have large power storage backups, using, for example, lead acid batteries, as well as frequency smoothing. Flywheels and ultracapacitors are also finding application for grid frequency regulation in such critical applications, as utilities commonly vary the frequency to smooth the power output. Some essential service industries, such as the telephone industry rely mainly on large batteries for backup in case of power failure. In remote areas, such as Fairbanks, AK, a 40-MW Ni/Cd battery system is used to guarantee continuous power availability.

In the last decade, there has been renewed attention given to electrifying the transportation sector; electric vehicles dominated transportation for a short period at the beginning of the 20th century. Initiated by the success of the Toyota Prius hybrid electric vehicle, the all-electric Nissan Leaf and the plug-in GM Volt have entered the market. The hybrid bus has entered the fleet, with well over 25 million miles driven using Li-ion batteries. Both the GM Volt and the buses have an all electric drive, with the internal combustion engine driving a generator. All these vehicles gain efficiency by recovering energy through regenerative braking. A related application is the capture of the energy normally wasted when a dock crane is lowering a crate; capturing this energy through capacitors saves around 40% of total energy utilization. Similarly, subway trains, with many stops and starts, can capture the braking energy for future use. In all these transportation applications, low cost and long life are essential for commercial success.

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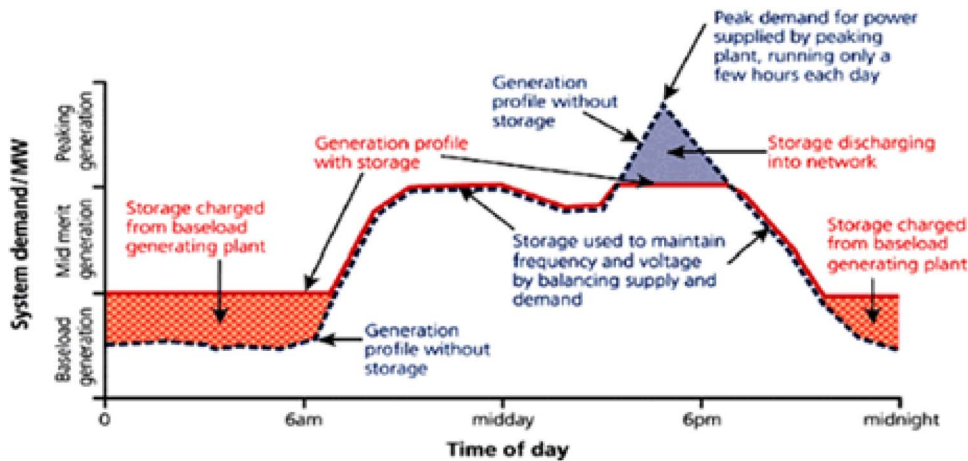


Fig. 1. A typical electrical power profile, showing the large variations during a 24-h period. In a load leveling scenario, an electrical energy storage device would be charged during low-power demand periods, and would discharge during high-power demand periods, thus filling in the valleys and lopping-off the peaks. A utility would need less overall power generation capability, and could delay the installation of extra generating capacity.

Renewable energy sources, such as wind and solar, cannot be the sole provider of energy without an associated energy storage facility. Even when they are plugged into the grid, a storage device is required to smooth the output; an example is the new West Virginia wind farm, which has an associated 20-MW battery storage facility [3]. Moreover, when the input into the grid from renewable sources exceeds about 10%, energy storage will be required. In addition, wind power is most prevalent in the overnight hours when there is the lowest demand for power. A large storage facility could also ameliorate the need for intermittent power generation sources to cover peak demand. A typical electrical demand profile is shown in Fig. 1. If a low-cost energy storage system were available, the prime power generator could be run through the night filling the storage device, whose energy could be released during the peak demand hours, eliminating the need for peak-only power stations.

II. TYPES OF ENERGY STORAGE

The lowest cost energy storage system is pumped hydro in which water is pumped uphill into “lakes” when excess generating capacity is available and then allowed to flow downhill through the pump turbines during high peak demand. The round trip efficiency is around 70% (energy out/energy in) with today’s turbines. Probably the first pumped hydro facility was at Schaffhausen, Switzerland, which started up around 1909; it produced around 1 MW of power. A larger system at Blenheim-Gilboa, NY, can now generate over 1.1 GW of power, after the 40-year-old turbines were replaced [4]. Even larger is the Raccoon Mountain facility of the Tennessee Value Authority (TVA) [5], [6], which can produce reliably 1.6 GW of power for

almost a whole day; the water drops 990 ft from the upper reservoir to the turbine pumps. It takes 28 h to fill the reservoir on top of the mountain, and the reservoir covers 528 acres, with a dam 230 ft high and 8500 ft long. It is the largest rock-fill dam built by the TVA. The largest pumped hydro facility in the world is in Bath County, VA, with a capacity of 3 GW [7]. Presently, there is around 25 GW of capacity in the United States at around 250 locations; this is just 2.5% of total generating capacity. There are, however, very limited locations remaining where water pumping can be installed, and it is unlikely that any more will be built in the United States, where dams are being removed rather than built. However, if the system could be buried out of sight, then opportunities might open up. One such example is found in the Snowdonia mountains of Wales at Dinorwig [8]. This system has 288 MW of power output.

A variation on water pumping is to use compressed air either alone or in combination with natural gas combustion. The latter type of system has been in successful operation in Huntorf, Germany, for more than 20 years, and is now being used to store energy from wind power [9]. One other such system is in commercial use in McIntosh, Alabama, and it uses off-peak power to compress the air; it only uses one third of the natural gas of a conventional natural gas plant [10]. A pure compressed air energy storage system (CAES) has been in the planning stage in Iowa for some time, with no indication that it will be built; the plan was to use wind and off-peak power to compress air. Here again the technology is limited by the availability of suitable caverns. So we must look elsewhere for solutions to provide distributed storage.

Pumped hydro and compressed air systems store energy using potential energy. In contrast, flywheels store

energy by kinetic energy. The faster they spin, the more energy they store. Flywheels are beginning to find application for frequency smoothing where long-term storage is not required. They tend to use carbon composites, and many flywheels can be gathered together to provide high output. One such prototype system in Stephentown, NY, which started operation in 2011, has a 20-MW output with a storage capacity of 5 MWh, so it can provide maximum output for 15 min. It uses 200 flywheels. However, the developer Beacon Power went bankrupt, but the buyer intends to keep the facility running as it is reported that the facility is cost effective. However, it is not clear that very large systems are feasible, due to safety issues that might demand that the flywheels be in strong bunkers.

In some special cases, load leveling is economically viable today using batteries. A 1-MW sodium/sulfur battery system was used on Long Island, NY, to provide power during peak periods for compressors for 220 natural gas buses. An 8-MW going to 20-MW Li-ion battery facility is in place in Binghamton, NY, for smoothing grid power and for brief power supply [11]; its cost is around \$23 million. At these cost levels, large installations need to be cited where electricity is the most expensive and Long Island is considering a 400-MW facility.

This paper will be mainly concerned with batteries and capacitors, but there are a number of other energy storage opportunities. Fuel cells are a source of energy, and are best described as primary batteries as they usually are not normally rechargeable and therefore are not applicable for repetitively storing energy. However, metal air batteries have several features in common with fuel cells, and as they show some promise as future storage systems, their history and features will be considered along with batteries and capacitors as all are based in electrochemistry. Whereas batteries store energy, capacitors are best thought of as storing power. This is made clear in Fig. 2, which compares the storage capabilities of several systems. In addition, the quality of the energy from capacitors is generally poor, that is, the voltage delivered is a strong function of the state of discharge whereas batteries tend to have a fairly constant output voltage. Fuel cells, operating on liquid fuels such as methanol, can have high energy storage but their power output is limited. Similarly, Li-oxygen batteries also may have (more later) high energy storage but their power output will be low. Moreover, their efficiency is optimum only at constant output and their poor response time demands that they be coupled to a storage medium such as batteries.

As can be seen from Fig. 2, none of these storage media approach the storage capacity of oil. To place in perspective energy storage, a car can drive 20–30 mi on a gallon of gasoline, whereas a small car can drive 4 mi on a kilowatt hour of electricity, so 5–7 kWh are equivalent to 1 gal. At an energy density of 100 Wh/kg, around 60 kg of batteries are equivalent to 1 gal of gasoline, which weighs 6.2 lb.

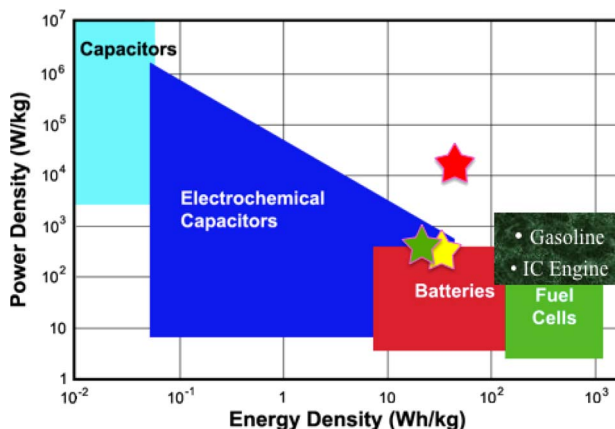


Fig. 2. Comparison of the power versus energy density characteristics of a number of storage media. Three commercial examples are already shown: yellow star—2008 Toyota Prius; green star—BAE Bus; red star—A123 Formula 1 race car booster.

III. WHAT ARE BATTERIES AND CAPACITORS?

There are two dominant kinds of electrochemical energy storage: batteries and capacitors. In a battery, electrical energy is stored as chemical energy whereas in capacitors energy is stored as surface charge. Thus, the attributes of the materials must be quite different. In batteries, the chemical reactions occur throughout the bulk of the solid, and so the material must be designed to allow the ingress of the reacting species throughout the material and to allow its subsequent removal. This must occur thousands of times to provide a commercially viable rechargeable battery. In contrast, for a capacitor, large amounts of surface are required, the storage capacity being directly related to the surface area. As the structural integrity of a capacitor material is not challenged, pure capacitors can be charged and discharged millions of times without any significant degradation of the materials, whereas in batteries, the chemical reactions are not always readily reversed because structural changes of the materials occur. Supercapacitors are a hybrid between the two, involving both surface charge and some Faradaic reactions in the bulk of the material.

Batteries and capacitors contain two electrodes, the anode and the cathode, as shown schematically in Fig. 3. The anode is the electropositive electrode, from which the electrons flow on discharge; the cathode is the electronegative electrode to which the electrons flow through the external circuit doing work. To balance this flow of electrons, normally cations flow through the electrolyte in the battery from the anode to the cathode. This electrolyte, which may be a liquid or a solid, only allows for the flow of ions and not electrons. It is typically an aqueous solution, such as sulfuric acid in the Pb-acid battery or potassium hydroxide in water in the case of the common Zn/MnO₂

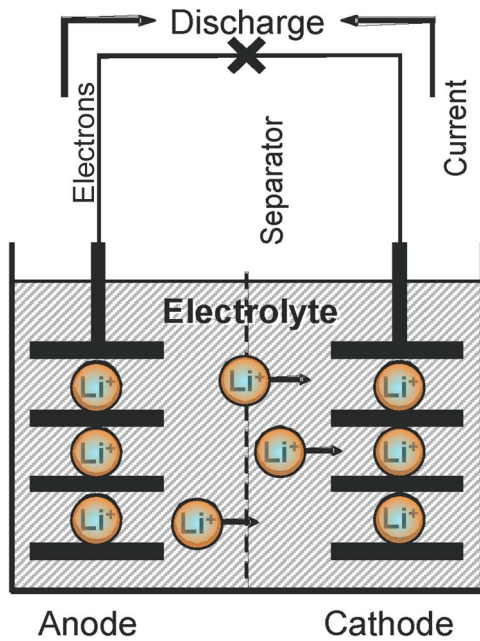


Fig. 3. Schematic of a battery.

dry cell. To ensure that the two electrodes do not touch each other, a porous separator is placed between them. It is conventional in the battery/capacitor area to describe the more electropositive electrode in the charged state as the anode, irrespective of whether the system is being charged or discharged. The reaction mechanism of a modern battery and the complexity of a real electrode will be discussed below in the second age period.

IV. FROM 19TH CENTURY TO PRE-1970s

Batteries are by far the most common form of storing electrical energy, and range in size from the button cells used in watches to megawatt load leveling applications. They are efficient storage devices, with output energy typically exceeding 90% of input energy, except at the highest power densities. The first battery was Volta's cell (1800) that had alternating discs of zinc and copper separated by cardboard and using a brine solution as the electrolyte. This is the same cell that young scientists build today using a lemon as the electrolyte. The Volta cell evolved into the Daniel cell (1836) that had two electrolytes, and then into the Leclanche cell (1866) that used a zinc anode and a carbon anode. The present small dry cell using an alkaline electrolyte, a zinc anode, and a manganese oxide cathode was not invented until 1949. These are all primary cells, and not usually rechargeable. Rechargeable, also known as secondary, batteries have evolved over the years from lead acid (Gaston Plante in 1859) through nickel-cadmium (1899) and nickel-metal hydride, NiMH, (mid-1980s) to Li ion (1977). Ni-Cd batteries have been and are still extensively

used in high-power consumer devices, such as gardening tools, electric razors, etc., and still are used as the starter batteries for aero engines. They are likely to be displaced from consumer applications by Li ion, because of the toxicity of cadmium.

V. FROM THE 1970s TO THE PRESENT

There was a surge of interest in the 1970s in developing new rechargeable batteries. In 1967, scientists at the Ford Motor Company discovered [12] that sodium beta alumina had an exceptionally high ionic conductivity; this discovery was the prelude to a revolution in solid-state electrochemistry [13] that resulted in the use of solid compounds that could reversibly store lithium, like TiS_2 , or hydrogen, like LaNi_5 , which became the basis of the rechargeable Li-ion batteries and the NiMH batteries, respectively. The successful commercialization of the sodium-sulfur battery took around 40 years, after extensive research efforts predominantly in Europe, with NGK of Japan taking the battery to market. This battery operates at over 300°C , with the sodium and sulfur reactants being in the molten state; they are separated by the beta alumina ceramic in the form of tubes or plates. Such batteries are typically being used for stationary load leveling applications, and are up to 200 MW in power. One such application is that on Long Island discussed above. A variant of the Na/S battery is the Zebra cell, developed in South Africa. In this cell, the cathode comprises, for example, a mixture of sodium chloride and nickel, which on charging deposits sodium at the anode and nickel chloride at the cathode. This cell has the advantage of not handling sodium metal during the manufacturing process. It is presently being actively commercialized by General Electric (GE) in Schenectady, NY, for stationary applications.

Extensive research on rechargeable lithium batteries operating around room temperature began in the early 1970s, when it was discovered that intercalation reactions were ideal for storing energy. So what is intercalation? Intercalation is the insertion of a leap day into some calendar years to make the calendar follow moon phases. In chemistry, intercalation is the reversible insertion of an ion or a molecule into a crystalline lattice without any significant change of that lattice except for a minor expansion or contraction. Around 1970, there was much interest at Stanford University (Stanford, CA) in changing the physical properties, such as conductivity and specifically superconductivity, of materials by intercalating ions or molecules into the host material's structure [14]. The dream was to engineer the desired properties by a simple insertion of electron donors or acceptors into the host lattice. Although that work showed that the superconducting temperature could be changed, the key scientists had moved East to Exxon and Bell Laboratories in New Jersey. There, the discovery was made that these intercalation reactions could evolve a lot of energy, in fact sufficient to

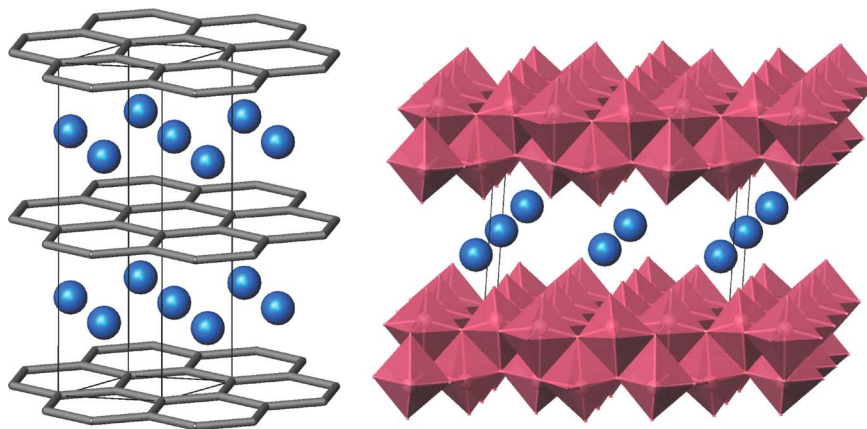


Fig. 4. Two intercalation compounds: (left) C_6Li and (right) $Li_xV_4O_{10}$. Blue shows the Li ions. In a Li-ion battery the Li ions are shuttled between such two compounds.

be of interest for storing energy. The competition between the two laboratories continued for the next ten years—the first golden age of lithium battery research and development. Today essentially all secondary lithium batteries use intercalation reactions [15] at both electrodes as the basis for storing energy, so the basic technology has not changed in almost 40 years.

Examples of intercalation reactions are the insertion of lithium into layered TiS_2 [$Li_xTiS_2(0 \leq x \leq 1)$], of lithium into V_4O_{10} , and of lithium into the layers of graphite giving LiC_6 . Fig. 4 shows two examples of lithium intercalation into host lattices. It is the former reaction that I and my colleagues at Exxon found to have an energy of reaction corresponding to around 2.5 V, and formed the foundation of the first rechargeable lithium batteries. This Li_xTiS_2 intercalation compound is now the ideal example of intercalation, showing complete solubility of lithium for all values of x from 0 to 1—so no energy is lost in forming a new phase. Fig. 5 shows how the cell voltage changes continuously for such single-phase reactions.

The cathode in the common alkaline cell MnO_2 also is reduced by hydrogen by an intercalation reaction forming $MnOOH$, rather than Mn_2O_3 as originally thought. Researchers at Philips (Eindhoven, The Netherlands) discovered that the $LaNi_5$ compound could readily insert six atoms of hydrogen forming $LaNi_5H_6$. This revolutionized the Ni/H_2 battery as this reaction occurred closed to atmospheric pressure in contrast to the high pressure used for cylinders of hydrogen. This technology was commercialized into the NiMeH technology we know today. They were the initial workhorse for electronic devices such as computers and cell phones. They have almost been totally displaced from that market by Li ion because of the latter's higher energy storage capability and for the last decade lower cost. The NiMeH technology was the battery used in the first generation of hybrid electric cars, such as the Toyota Prius. It is highly reliable, cycling several thousand

times. However, it is being displaced by the higher energy and now lower cost lithium batteries in today's generation of hybrid and electric vehicles, such as the Nisan Leaf, GM Volt, BAE buses, and the next generation of Prius.

The efforts at Exxon in the 1970s resulted in cells as large as 45 Wh, as indicated in Fig. 6. These cells used dioxolane as the electrolyte solvent because it allowed the cycling of all of the lithium in the lithium anode more than 100 turns. However, it used lithium perchlorate as the electrolyte salt, which is not stable. In the Fig. 6 cells, the perchlorate was replaced by tetramethyl boron $(CH_3)_4B$, which was not as good at plating out lithium. There have been marked changes in lithium batteries since the early

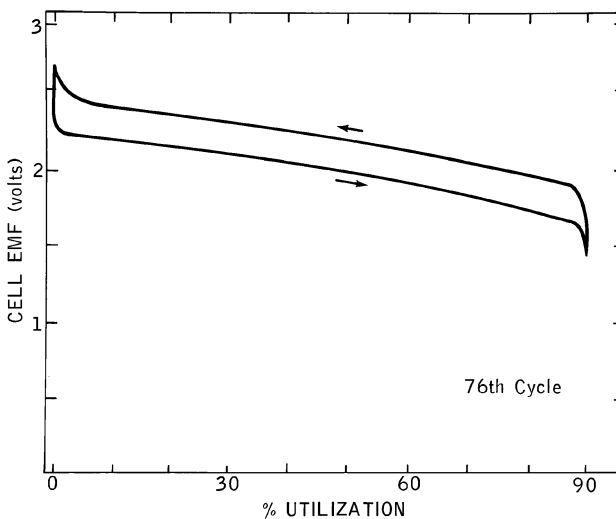


Fig. 5. Potential composition plot for a single-phase electrode reaction such as Li_xTiS_2 showing the continuous change of cell voltage with composition. This figure shows the 76th cycle at 10 mA/cm^2 using no carbon conductive diluent.

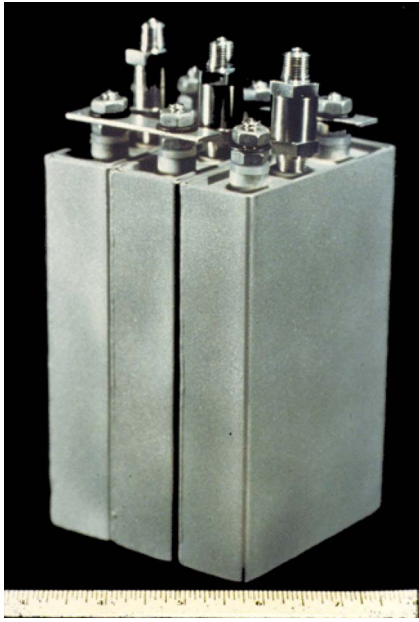


Fig. 6. An Exxon LiTiS_2 rechargeable lithium battery exhibited at the Chicago electric vehicle (EV) show in 1977. This cell used a tetramethylboride salt in dioxolane solvent electrolyte and each cell had a capacity of 45 Wh. It had pressure relieve valves, to ensure no pressure buildup.

1970s. The original Exxon LiTiS_2 batteries used pure lithium as the anode, but the plating of lithium is problematic with dendrites being formed (see Fig. 7) that can short out the cell and lead to fires. AT&T found this out when deploying Avestor's batteries that used a lithium anode, a vanadium oxide cathode, and a polymeric membrane; the result of such a fire is shown in Fig. 8. Exxon recognized this, and used a lithium–aluminum alloy as the anode [16]. This alloy was formed *in situ* by laying a sheet of lithium on top of aluminum; in the final stage of battery



Fig. 7. Lithium dendrites being formed on electrodeposition of lithium, from [18].



Fig. 8. The result of an Avestor battery fire in an AT&T system.

construction, prior to sealing the cells, electrolyte was added and this enabled the reaction between the sheets to form LiAl . This alloy loses much of its capacity after ten cycles, but this was sufficient for testing in initial applications such as powering light-emitting diode (LED) displays in devices such as watches. LCD displays, with their much lower power consumption, did not require frequently recharging the battery. The use of this alloy was the first use of materials that allow the shuttling of lithium between the anode and cathode materials without pure lithium ever being present. Such batteries are now known as Li-ion batteries. A carbon-based anode has been used in essentially all lithium batteries since 1990 [17]. Carbon can react with lithium to form the intercalation compound LiC_6 very readily at room temperature (see Fig. 4), and most recently purified natural graphites have replaced the expensive synthetic carbons, such as MCMC. This was probably the most important breakthrough that made the Li-ion battery commercially viable in the early 1990s, besides the perseverance of SONY's management.

As noted above, carbon is still the basis of Li-ion batteries today, but it is possibly the largest impediment in increasing the energy storage capability of these batteries. The carbon anode takes up as much space as the cathode, because of its low gravimetric density; its storage capability is 340 Ah/kg, but only 740 Ah/L. In addition, high rate charging is precluded because lithium deposition might occur that could lead to dendrite formation and subsequent shorting of the cell. By comparison, pure lithium has a capacity of 3800 Ah/kg and 2000 Ah/L. However, as noted above, no solution has been found in the last 40 years to electroplate lithium without dendrite formation. In addition, even if pure lithium is used, at least a threefold

excess must be used to attain 1000 cycles, because it will be very difficult to achieve better than 99.9% lithium deplating/plating efficiency [19], [20]. This will clearly reduce the above effective capacities by a factor of three, but these are still much higher than carbon-based systems.

The carbon-based anodes have to be improved if the storage capability of batteries is to be improved. Initially, lithium was alloyed with metals such as aluminum, which forms a one-to-one alloy LiAl with a very large theoretical energy storage capability (780 Ah/kg). However, the volume of the aluminum increases by 200%, which results in electrode crumbling, loss of electrical contact between particles, and rapid capacity loss. Moreover, pure aluminum has not been found to be compatible with carbonate-based electrolytes, so little work has been pursued. However, in the last decade, there has been renewed interest in metal-based anodes that are nanosized and can tolerate these expansions. A clue to the use of aluminum is to alloy it with a small amount of silicon [21]; this allows capacities of around 700 Ah/kg to be retained for more than ten cycles. This capacity is 50% higher than with silicon-free aluminum, and moreover, it is achieved using a readily available Al–Si eutectic alloy used in engine blocks.

Two other metals are being extensively studied as potential hosts for lithium; both tin and silicon can react with more than 4 Li/metal and the reaction is reversible. However, to retain the capacity on cycling, the metals must be nanosize. The first commercial application was in SONY's Nexelion camcorder battery pack [22]; the volumetric capacity was increased by 50% over the conventional battery. The anode in this cell is an amorphous Sn–Co alloy buried in carbon and containing some titanium [23]; it cycles well but is not viable for large batteries because of the cost of the cobalt. The Sn–Co exists as 5-nm particles encapsulated in carbon (Fig. 9), which probably prevents much contact between the electrolyte and the metal. Such contact would lead to large amounts of what is called the Solid Electrolyte Interphase (SEI) layer. The SEI layer protects the anode from chemically reacting with the electrolyte, and is an essential component of any lithium battery. The anode electrolyte combination is not in thermodynamic equilibrium, and this protective layer hinders undesirable reactions. However, if the anode changes volume on cycling, then the layer will be broken on expansion and will need to be rebuilt on each electrochemical cycle. Carbon forms a stable SEI layer and that is why it has been so successful. The knowledge gained from studies on the SONY Sn–Co anode has led to much research on both tin and particularly on silicon. There are now clues that the cobalt can be replaced by iron, which forms a range of compounds with tin; nanosized $\text{Sn}_2\text{Fe/Sn/Ti/C}$ combinations appear to perform well [24]. A warning is in order here, as in the preferred combination of Sn and Fe no iron was intentionally added to the reaction medium; the iron came solely from the grinding media, and this might have enabled a slow reaction to occur to form the optimum

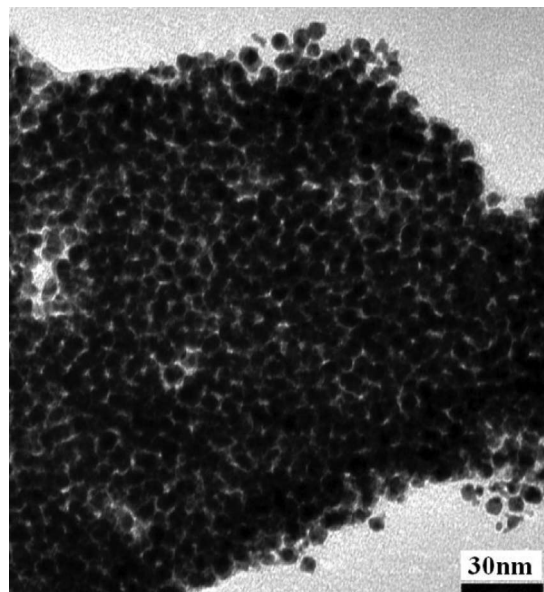


Fig. 9. Transmission electron microscopy of the SONY Nexelion anode [23].

morphology. A new Sn_5Fe compound also has interesting properties [25], but all of these compounds suffer from what is called first cycle lost capacity, which can be as high as 50%. This is a result of the charging capacity, lithium insertion, being much larger than the discharging capacity, lithium removal. It is thought to be due to the formation of the SEI layer, as well as to the very reactive surfaces of the metals and the amorphous carbons formed when the compounds are synthesized, typically by mechanochemical process (aka grinding). The efficiency of cycling approaches 100% after a few cycles.

Silicon has received much more attention in the last five years than any other host metal for the anode. It is readily available, low cost, and reacts readily with lithium under ambient conditions. As with tin, it needs to be nanosized to be effective; in addition, smart nanostructures need to be constructed to allow for both the huge expansion on lithium reaction and at the same time to attain high volumetric capacities. Fig. 10 is a schematic of why nanosized silicon is desirable [26]. Numerous announcements have been made about commercializing silicon anodes, but none are available yet, and Panasonic delayed its exciting 18650 cell until 2013. This cell has specifications showing a volumetric energy density 60% higher than today's 18650 cells; more on this will be presented in the next time period.

Back to cathodes. After the announcement and brief commercialization of Li/TiS_2 cells, there was a hiatus until 1990 when SONY brought onto the market the C/ LiCoO_2 cell. Whereas the commercialization of the Na/S battery took close to 40 years, the successful commercialization of the lithium secondary battery took less than 17 years.

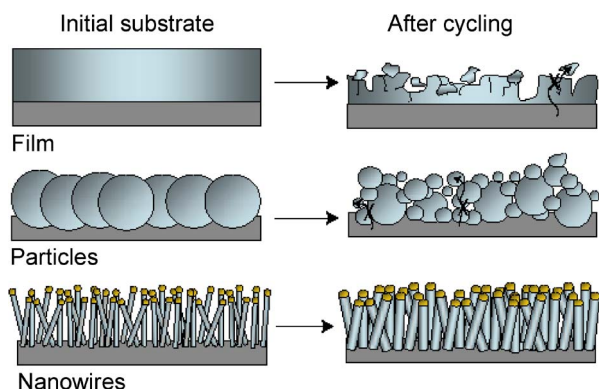


Fig. 10. Schematic of the reaction of lithium with silicon, showing three scenarios. In a film or a foil, after multiple lithium insertion and removal, the foil cracks and pieces flake off. In a particulate powder, the particles break apart forming smaller and smaller particles. In contrast, nanosized wires of silicon will simply expand filling the void space between each fiber. After [26].

Goodenough, who was studying the magnetic behavior of layered oxides at Oxford University (Oxford, U.K.) recognized that the structure of LiCoO_2 was similar to that of LiTiS_2 and might make an effective cathode material [27]–[29]. Indeed it did, and SONY licensed the technology from the U.K. Atomic Energy Authority and as they say the rest is history. LiCoO_2 was the dominant cathode material until about five years ago. Relative to TiS_2 , it has the advantage of a higher voltage (3.8 V), is easier to be handled (less air sensitive), and cells can be readily built in the discharged state as the cell potential is too high for the lithium to react with water. This last removes the need for the use of lithium metal in the manufacturing process. Even though LiTiS_2 can be built in the discharged state [30], [31], the lower potential means that thermodynamically it can react with oxygen and water with lithium removal. Its disadvantages are that a conductive diluent, such as carbon black, must be added which reduces its volumetric capacity and rate capability as reaction can only occur at the

intersection of three phases: the electrolyte, the carbon, and the LiCoO_2 particles. In addition, the structure changes with lithium content, so care must be taken not to remove too much lithium or reorganization of the layers will occur with subsequent structural disorder and capacity loss. LiCoO_2 has what we call a three-sheet structure, where in stacking the CoO_2 sheets, each is staggered one third relative to the neighboring ones giving a single-sheet repeating structure. However, in CoO_2 itself, the sheets are stacked directly one above, just as in Li_xTiS_2 for all values of x . In structural language, the oxygen atoms in LiCoO_2 are cubic close packed whereas in CoO_2 and Li_xTiS_2 the anions are hexagonally close packed. Another reason for not removing all the lithium from the cobalt oxide is the inherent instability of the Co^{4+} in CoO_2 . SONY [32] used large particles, 15–20 μm , of LiCoO_2 to mitigate against surface reactions initiating thermal runaway, and had an excess of lithium in the compound, $\text{Li}_{1+x}\text{Co}_{1-x}\text{O}_2$. Table 1 compares these two cathodes with each other and with LiFePO_4 (more later on the last).

Although the LiCoO_2 cathode has dominated for well over a decade, there has been much effort to replace the cobalt, which is too expensive and the battery market is driving the price of cobalt. A wide range of metals can be used to replace either totally or in part the cobalt. The more common compositions are $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [34], [35] and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, commonly known as NMC and NCA, respectively. The NCA composition has a higher capacity, but is less thermally stable giving off heat as low as 200 °C when in contact with the electrolyte so thermal runaway is a real concern with it. Aluminum or magnesium is always present in the structure, so that all the lithium cannot be removed as NiO_2 is thermodynamically unstable except under high oxygen partial pressures. The NMC does not release heat until around 350 °C so is much more stable and has displaced at least part of the LiCoO_2 in batteries for electronic devices. It is not clear that the equimolar composition is the optimum composition. In both of these compounds, most of the electrochemistry occurs on the nickel ions using the redox couple

Table 1 Comparison of the Three Cathode Materials LiTiS_2 , LiCoO_2 , and LiFePO_4

Property	LiTiS_2	LiCoO_2	LiFePO_4
Number of phase	1	Multiple	2 (maybe 1)
Change in Li content	1	0.5	1
Capacity, Ah/kg	213	137	169
Cell voltage	2.2	3.8	3.45
Energy stored, Wh/kg	469	520	586
Energy stored, Wh/l	1.5	2.5	2.0
Electronic conductivity	Semi-metal	Semiconductor	Insulator

Table adapted from ref [33]. All values only consider the active material; the conductive carbon additive and binder are not included. The LiTiS_2 does not require any carbon additive; this will increase its storage capacity by 10-20% relative to the others. No weight is assigned to the anode.

$\text{Ni}^{4+}/\text{Ni}^{2+}$, with limited participation of the $\text{Co}^{3+}/\text{Co}^{4+}$ couple, and manganese stabilizes the lattice and remains as Mn^{4+} throughout the electrochemical process. The role of the cobalt is to help in increasing the electronic conductivity, and to minimize the number of nickel ions that migrate to the lithium layer. This latter leads to loss of capacity and rate capability, but a few percent (2%–3%) helps stabilize the layers like pillars in a room, so that they cannot move relative to one another. These cathode materials are drop-in technology for the existing cobalt systems, so spread through the market without knowledge except that the battery lasts longer on each charge as both have superior capacities to LiCoO_2 , around 20%+. So we see 40 years for Na/S commercialization, under 17 years for Li ion, with continuing incremental improvements of Li ion over the years. The energy density of commercial cells using LiCoO_2 have far more than tripled since their introduction in 1991; in just the five years from 1999 the volumetric energy density increased from 250 to over 400 Wh/L [36]. It increased further to 570 Wh/L in 2010 and the recently announced 18650 cell of Panasonic will have a capacity of 919 Wh/L using a Si-based anode and an undisclosed cathode.

Researchers continue to look at variations on the above layered materials to increase the capacity, rate capability, and cycle life. One example is increasing the lithium content as in $\text{Li}_{1+x}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2]_{1-x}\text{O}_2$; such materials appear to be used commercially where x is not much more than about 5%. Another example is to use extra manganese as well as lithium, as exemplified by the formula $\text{Li}_2\text{MnO}_3\text{LiMO}_2$, where $\text{M} = [\text{Mn}, \text{Ni}, \text{Co}]$, which researchers at Argonne National Laboratory (Argonne, IL) report can achieve capacities exceeding 250 Ah/kg [37]. However, there are a number of challenges in making such materials operative. First, they must be charged to 4.6 V on the first cycle when Li_2O is removed from the Li_2MnO_3 by evolution of oxygen at the cathode component, and plating of lithium at the anode. It still has not been confirmed whether the evolved oxygen attacks the electrolyte, but undoubtedly the oxide lattice will become disordered as the metal ions must diffuse into the particles to allow the evolution of oxygen on the surface. This results in poor rate capability and in the slow conversion of the material into a spinel-like phase, which leads to voltage fade on cycling. In addition, a recent study [38] on a compound synthesized from equimolar amounts of Li_2MnO_3 and $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ with an overall composition $\text{Li}_{1.2}\text{Ni}_{0.16}\text{Mn}_{0.56}\text{Co}_{0.08}\text{O}_2$ confirmed the poor rate capability showing that the capacity is lower than that of NMC at a C to 2C rate. It was also found that these materials have a poor thermal stability that is comparable to that of NCA and 100 °C lower than that of NMC compositions. At the present time, these Mn- and Li-rich compounds do not appear to have any superior characteristics to NMC and NCA, and emphasis is likely to be placed on further improving the NMC and NCA materials.

A related system is the manganese oxide spinel LiMn_2O_4 , which on charging gives Mn_2O_4 . It has a low capacity, but it is finding application in power tools and as a component in vehicle batteries because it has high rate capabilities and is inherently low cost. It was also considered for safe high rate hybrid electric vehicle (HEV) batteries, when coupled with the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, to give a 2.5-V battery. However, large cells containing the titanium spinel have been found to generate hydrogen gas and swell.

In 1997, Goodenough disclosed another new cathode [39], the olivine class of compounds of formula LiMPO_4 , where M is Fe, Ni, Co, Mn, or a combination of them. The iron compound generated a lot of interest because of its potential low cost. It was not long before these compounds appeared in commercial products [40], such as power tools, and then for transportation such as buses, e-bikes, and personal transporters, and for large load leveling systems. This material being an electronic insulator posed a distinct problem. In commercial cells today nanosized materials, < 100 nm, are covered with a carbon coating or are ground to give a conductive carbon cover. In many cases, where the material is made at about 650 °C or above in a reducing atmosphere, the material will be slightly reduced by the gas or by the carbon giving a conductive iron phosphide coating, Fe_2P . All this further reduces the volumetric storage capacity, so that its storage capability is much lower than that of the layered oxides even on a weight basis, as shown in Fig. 11. Thus, LiFePO_4 is not finding application in volume constrained applications such as portable electronic devices and cars. It is dominating in larger vehicles, such as buses, and in grid systems. In the latter, mobile storage systems such as that in Johnson City, NY, shown in Fig. 12, can defer the need

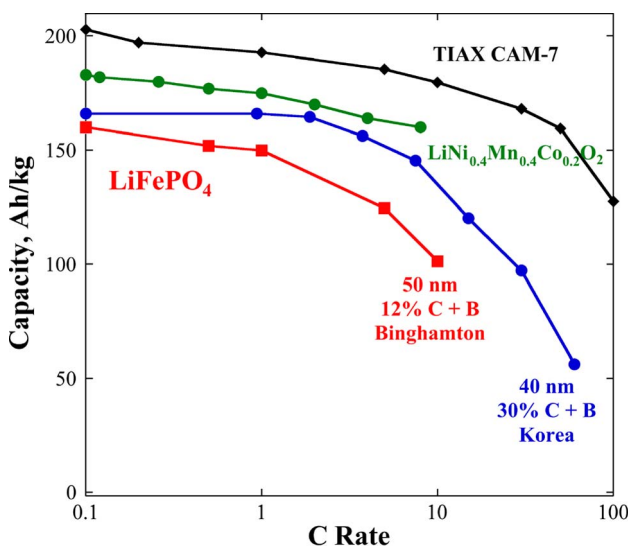


Fig. 11. Comparison of the laboratory cell capacity of the layered oxides with the olivines, after [33]. The oxides have higher capacities at all rates. The difference is even greater for the volumetric capacities.



Fig. 12. Energy storage system in Johnson City, NY, uses LiFePO_4 cells. A similar system has also been installed in West Virginia to smooth the power from the Laurel Mountain wind farm.



Fig. 14. A British Airways staff bus is totally electric, and uses regenerative braking. Courtesy of Globe News wire service.

for substation upgrades. This system is used for frequency smoothing and short-term power supply. Today, these contain thousands of cylindrical cells; in the future, prismatic (flat plate) designs are likely to be used. Similar cells, packaged in modular packages, are used in the BAE Systems buses [41], as shown in Fig. 13; the battery and control system are sited on top of single-decker buses, and at the back of the upper deck on the London double-decker buses. Full electric buses are also now being powered by LiFePO_4 batteries [42] with a daily route of 50–60 mi, as indicated in Fig. 14.

From a scientific point of view, the LiFePO_4 electrode is intriguing because despite being an insulator, and reacting by a two-phase mechanism, it shows one of the highest reaction rates of all cathode materials when nanosized.



Fig. 13. Part of the London fleet of all-electric drive HEV buses [41].

Fig. 15 shows the flat discharge/charge plateau typical of a two-phase reaction [43]. One suggestion [44] is that no nucleation of a second phase occurs, but in very small particles, a small over-potential of 20–40 mV is sufficient to cause the reaction to occur by a single-phase mechanism. The exact mechanism in this very different material is still the topic of extended research, and its understanding might lead to improved materials.

Nickel metal hydride batteries have been under development almost as long as lithium batteries, and came to market slightly earlier. They are also based on intercalation chemistry with the hydrogen being held in solids such as the LaNi_5 class of material. They use the same Ni electrode as Ni/Cd batteries and are built on that technology; however, that also carries with it the memory effect of the Ni electrode. They dominated the first generation of portable electronic devices, having higher energy densities but lower power capabilities than Ni/Cd. They in turn have

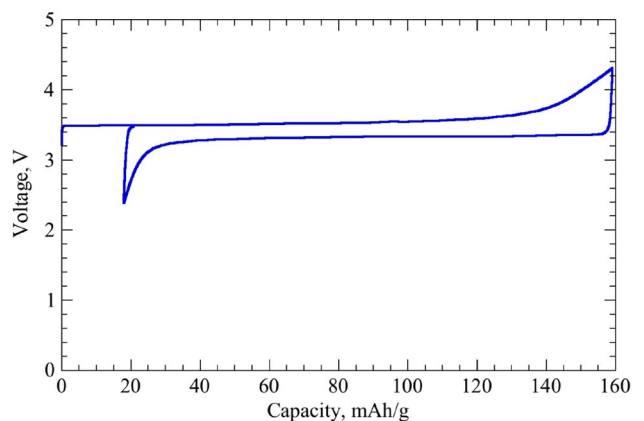


Fig. 15. Cycling curve of the olivine LiFePO_4 showing the flat plateaus indicating that the two phases LiFePO_4 and FePO_4 are present except at the composition extremes [43].

now been almost totally displaced by Li-ion batteries in such applications, because of the latter's doubled storage capability and lower cost. They are beginning to displace primary alkaline cells for low-end cameras and such devices. They found a very successful market in the first-generation hybrid electric vehicles, such as the Toyota Prius, because of their excellent cycle life and safety characteristics and are likely to remain dominant in that area. However, they are not viable for plug-in hybrid electric vehicles (PHEVs), except for very limited range vehicles, or full electric vehicles (EVs) because of their much lower volumetric energy densities.

Capacitors have to be considered as power sources rather than energy sources, as indicated in Fig. 2. They are often used in combination with batteries, for example, for some cases of regenerative braking to lower the stress of high-power pulses on a high-energy battery. The opposite is also true, when a battery is used to charge a supercapacitor in an active heart pacemaker. They have been used alone in HEV buses for regenerative braking, but are most effective on flat routes as sufficient storage for recovering braking on hills is not cost effective. They have found application in dockyards for recovering the power when cranes lower shipping containers, and in a commuter bus in Russia. The biggest challenge capacitors face is their cost, an order of magnitude higher than Li ion, e.g., \$3626/kWh versus \$300/kWh for the battery, but the reverse is true on a power basis, \$7.3/kW versus \$30/kWh for the Li-ion battery [45]. Thus, efforts on capacitors should emphasize their power capabilities, and their potential combination with high-energy batteries, not as energy storage devices themselves. Further reading can be found in a classical paper and a recent paper [46], [47].

Background reading on the present status can be found: batteries and fuel cells [48]–[50], energy storage [51], [52]. A more extended discussion with extensive background material may be found in a 2007 U.S. Department of Energy workshop on Electrical Energy Storage [51].

A. Where Will We Be in Ten Years?

Looking at the big picture, one might expect by 2020 that all vehicles sold will be hybrid of one kind or another. A simple hybrid system can conserve around one third of the fuel used. It is likely that many vehicles will be stop–start, that is, the internal combustion engine will switch off when the vehicle is stopped; that service will demand a more advanced battery than today's lead-acid starting, lighting, and ignition (SLI) battery. It is also likely that most systems in the car will be electrified, with the removal of most belt drives. All these changes will take time as the fleet turnover is more than ten years, and lower cost longer lived batteries will be required. Similarly, in the same timeframe, more renewable energy will be on the grid, and will almost certainly demand the associated storage. As noted earlier, this is unlikely to be pumped hydro for political and environmental reasons; compressed air is not expected to make a

significant penetration for the same reasons. We are thus left with batteries, capacitors, flywheels, and superconducting magnetic energy storage (SMES). There is little mention these days of SMES because of the technological challenges faced and the high cost, and it will not be further discussed here. Flywheels are likely to find application in niche markets for grid smoothing, but not for large-scale energy storage. If their cost drops sufficiently, and their perceived safety improves, they could find application for regenerative braking where they would be in competition with the next generation of supercapacitors. Thus, in the next decade, most of the advances will be found in batteries and supercapacitors. Rechargeable fuel cells are considered as batteries here. Though not discussed here, thermal storage is likely to find greater application. Today, some vehicles such as the Toyota Prius have a thermal storage pack that allows for more efficient startup. Solar thermal farms are likely to use enhanced thermal storage to allow electrical generation at the highest value time of day.

The U.S. Department of Energy has invested more than \$1 billion in energy storage in the last three years, ranging from manufacturing plants to fundamental research. The fundamental research effort is focused on a number of energy frontier research centers (EFRC); more applied but high risk research and development in the Advanced Research Projects Agency Energy (ARPA-E), which focus on efforts beyond Li-ion for both grid and transport applications. Finally, an energy storage hub will start up later in 2012. This is the second battery dream period, and major technical breakthroughs are to be expected.

The history of lithium batteries is not that old, in contrast to fuel cells that have been around since Grove described the first one in 1839 [53]. In just 40 years, two new battery systems, Li ion and Ni/MeH, have not only dominated the portable electronics business, but in many ways enabled it. They are now beginning to do the same for transportation, and Li ion has entered the electric grid market. These advances have all been based on the concept of intercalation reactions. How much further can intercalation chemistry be pushed? At a minimum, these cells will almost certainly displace Ni/Cd in consumer applications, as cadmium gets banned from sale. There is still much room for improvement in the storage capability of Li-ion cells, as the data in Table 2 indicate. These data raise the question: Where has all the energy gone?

Clearly there is much room for improvement. There is much dead weight and volume in today's batteries and supercapacitors; in addition the full capability of the active materials has not been attained. As noted earlier, the volumetric energy density of Li-ion batteries has increased from 250 to 570 Wh/L over the last decade. Panasonic projects that their new 18650 cell will increase it further when it goes to market. There is no reason to believe that the energy density cannot be increased further, possibly even as far as 50% on both volumetric and gravimetric basis within the next ten years. For almost all applications,

Table 2 Energy Densities of Some Lithium Battery Cells

Chemistry	Size	Wh/L theoretical	Wh/L actual	%	Wh/kg theoretical	Wh/kg actual	%
LiFePO ₄	54208	1980	292	14.8	587	156	26.6
LiFePO ₄	16650	1980	223	11.3	587	113	19.3
LiMn ₂ O ₄	26700	2060	296	14.4	500	109	21.8
LiCoO ₂	18650	2950	570	19.3	1000	250	25.0
Si-LiMO ₂	18650	2950	919	31.2	1000	252	25.2
Panasonic							

The theoretical values in the table assume only the active components, and no volume or weight for lithium beside that in the cathode.

the volumetric energy density is much more important than the gravimetric one. Further improvements will need significant changes in the materials used. In the above calculations, it has been assumed that only one lithium can be intercalated into the structure, but in a few cases, two lithium can be inserted. Some examples include Li₂MO₂ and Li₂VOPO₄, but there are some significant challenges. In the case of the layered oxides, there are insufficient sites in the structure for all the Li ions to reside on octahedral sites, so the MO₂ layers must shift to allow the second lithium to be intercalated. This will probably be detrimental to the long-term stability of the oxide. One way around this is to switch from lithium to magnesium, when only one magnesium ion needs to be intercalated so no change in structure would be needed. However, much effort will be needed to make a successful magnesium battery, including an anode and an electrolyte. The beginnings of such cells will be accomplished within ten years, but without significant breakthroughs it will probably not go commercial until 2020.

Within ten years, the carbon electrode will have been replaced by metal alloy systems, perhaps tin or silicon based. Significant effort will have been made on solving the lithium, and other metal—magnesium, zinc, and maybe even aluminum—electrode position. There is a finite probability that pure metals will be used in some liquid electrolyte cells by 2020. They find application today in all solid-state thin film cells.

After the success of lithium iron phosphate, there will be a search for other phosphates that can react with two Li ions or one magnesium ion. VOPO₄ has already been identified as one such candidate [54]. An in-depth computational study by the Ceder group [55] suggests that there are not many materials candidates. The results of that study are shown in Fig. 16. Two materials have an opportunity to achieve the 800-Wh/kg goal, the V³⁺/V⁵⁺ and the Mo³⁺/Mo⁶⁺ couples within the present electrolyte stability limit of 4.5 V. Such compounds will have been studied in the next five years, and probably not found capable of sustaining high capacities with lithium over hundreds of cycles. Other compounds may be possible if a high-voltage electrolyte is discovered. One such example is the pyro-

phosphate, Li₂FeP₂O₇, but today only one lithium can be used because the potential of the second level is over 5 V [56]. The use of magnesium might be more feasible.

Conversion reactions offer an opportunity to achieve much higher capacities than intercalation reactions. In conversion reactions, the structure is destroyed on reaction with lithium, and must be rebuilt on recharge. Such an example is the reaction between Li and FeF₂ giving 2LiF and Fe, or between Li and FeF₃ giving 3LiF and Fe. Extensively studied, these couples appear feasible [57], but there are severe challenges to be overcome including rates of reaction and minimization of the large hysteresis between the discharge and charge curves.

Related to conversion reactions is the chemistry involved in metal air and metal sulfur systems. As noted above, GE is on the point of commercializing the Zebra-type battery that operates at around 300 °C, which in the charged state contains molten sodium as the anode and metal halides, such as NiCl₂ as the cathode. These will find commercial markets in this decade, probably at the expense of Na/S, for mid-to-large-scale load leveling. They are expected to be lower cost than Li ion. The ambient

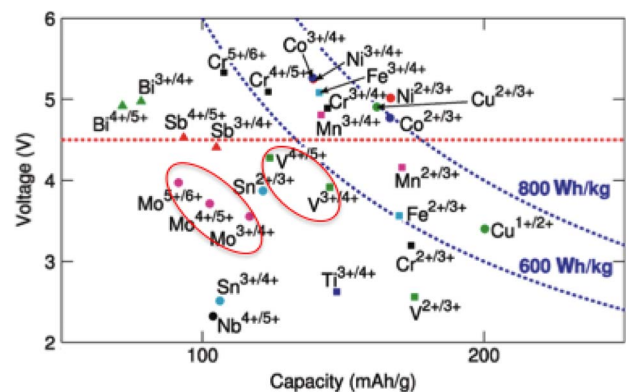


Fig. 16. The computational prediction of the cell voltages for a wide range of transition metal phosphates. Two couples are identified in the red ovals within the electrolyte stability limit of 4.5 V (red line). After [55].

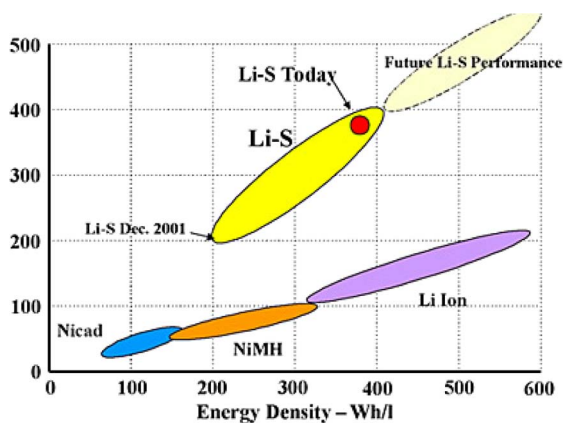


Fig. 17. Energy storage capability of lithium-sulfur cells compared to other cells, from [58].

temperature Li/S battery has been under development for more than a decade by Sion Power (Tucson, AZ) under license from Polyplus Corporation. Some cells are commercial and are used in some military markets for flight power today [58]. They already substantially exceed the gravimetric energy storage capability of Li ion, as can be seen from Fig. 17 [58], but as the figure equally shows, they have a much lower volumetric storage capability. BASF recently invested \$50 million in Sion Power, so it is likely the market will be much enhanced over the next decade particularly where weight and not volume is important. However, much effort will be required to increase the charging rate above the present specification of C/5 (5 h), and the volumetric capacity above the present 320 Wh/L, which is just one third that of the planned Panasonic Li-ion cell.

Metal air batteries, in particular Li-air, are receiving much research attention and have received much hype over the last few years. Will they play a role in energy storage in the next decade? The challenges are discussed below. Primary Zn-air is extensively used in hearing aid batteries; such batteries once opened to the air tend to react chemically and so have a limited lifetime whether used or not. Secondary Zn-O₂ cells are being actively considered, as zinc is the most electropositive element that can be plated from aqueous solutions without generation of hydrogen. These cells use a bifunctional electrocatalyst at the oxygen electrode to lower the energy to break the oxygen-oxygen bond on discharge and assist in the evolution of oxygen on charge. The air-electrode, typically carbon, must be porous to allow the oxygen and electrolyte in and must resist corrosion by the oxygen on recharge. This last is a major problem that all metal-oxygen batteries and aqueous-based fuel cells face and have not solved yet. Such a zinc battery typically operates at below 1.2 V, and is charged at close to 1.9 V, so they are very inefficient, much less than pumped hydro and lithium batteries. Most

metal-air batteries suffer from the same problems, and aluminum/oxygen rechargeable batteries are a dream of the future. The remainder of this discussion will focus on Li/O₂ rechargeable cells.

Abraham showed [59] in 1996 that a Li/O₂ couple was inherently rechargeable in a solid polymer electrolyte cell. Most of the work in the last five years has used the same electrolytes as in the standard Li-ion cells. The carbonate-based solvents in these cells have been conclusively shown to react with the lithium oxides formed in the reaction, in particular, the superoxide LiO₂ [60]. As of the end of 2011, no stable organic solvent had been found, but research continues. Most of the present effort has focused on the reaction of Li and O₂ giving the peroxide Li₂O₂, rather than the oxide Li₂O, where there are severe questions as to whether it can be recharged whereas the peroxide can be recharged albeit at around 4 V [61]. The discharge is just below 3 V, so here again the round-trip efficiency is not acceptable for most applications. As the oxygen-oxygen bond is not completely broken in forming the peroxide, some [62] have questioned the need for an electrocatalyst, suggesting that it may do more damage than good; it may be a better catalyst for the reaction of the peroxide with the solvent than for oxygen evolution.

The challenges facing commercialization of the secondary Li-O₂ cell are listed as follows.

- 1) They need a stable electrolyte.
- 2) The reactions occurring must be controlled, so that only the desired reactions occur.
- 3) The oxygen cathode electrocatalyst must be very selective to the desired reaction, and not promote undesired ones. A system must be designed where the insulating lithium oxide formed does not completely coat the electrocatalyst or the underlying carbon support, thus causing the reaction to stop.
- 4) The lithium must be protected from the oxygen electrode. No oxygen, nitrogen, water, or carbon dioxide should migrate across the electrolyte, even when standing over extended periods. A solid electrolyte separating the anode and the cathode compartments as used by Polyplus in their Li/sea water batteries is one approach [63]; see Fig. 18.
- 5) Electrodeposition of lithium without the formation of dendrites. This is a challenge facing all lithium and other metal-based batteries, and if solved could be used in today's Li-ion batteries to convert them over to Li batteries.
- 6) Containment of the electrolyte, if the oxygen electrode is open to the environment.
- 7) Improvement of the kinetics of reaction, which are much less than that of present-day Li-ion batteries.
- 8) Improvement of the overall efficiency of the charge/discharge process.

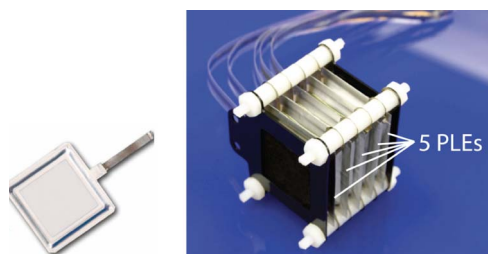


Fig. 18. (Left) The protected lithium electrode (PLE) used in the Polyplus primary Li-sea water cells, and (right) a battery made up of these cells. Courtesy of Polyplus.

These are formidable challenges, which are unlikely to allow the commercialization of a Li/O₂ battery in the next decade. It will take longer, but one has to answer the question: Is it worth the cost? What would a perfect Li/O₂ couple be capable of? Some simple back-of-the-envelope calculations can give some guidance. Table 3 compares Li-oxygen batteries with Li-ion batteries. The situation could be slightly improved if the reaction could go to completion, that is forming lithium oxide Li₂O. Not considered here are the weights and volumes of the electrocatalyst and porous carbon current collector. The latter is likely to take up significant volume because of the need of porosity to enable oxygen inflow; in addition, no allowance has been made for the air-handling equipment, and no allowance has been made for the higher packing efficiency of Li ion. Li-air cells are likely to be built like fuel cells with bipolar electrodes. To place these numbers in perspective, Polyplus's commercial lithium-sea water primary battery, shown in Fig. 18, has a storage capacity of 1300 Wh/kg and 700 Wh/L [63]. These values will not be exceeded in a rechargeable cell, as there is no product weight in the primary cells as the LiOH dissolves in the environment. Polyplus is targeting a value of 800 Wh/kg for their secondary cells: "Decade-old battery company PolyPlus is the poster child for a high risk, potentially game-changing ARPA-E target. The company is using the ARPA-E grant to build rechargeable lithium-air battery technology that it says can have an energy density of 800 Wh/kg. The secret sauce is in encapsulating the lithium so that it's a stable system. Developing that technology though into commercialization will take years (and already has taken years)" [64].

Table 3 Calculated Theoretical Energy Densities of Li-Peroxide Cells Compared with Li-ion Cells

System	Energy Density	Energy Density	Assumptions Made
	Wh/kg	Wh/L	
C-Lithium-ion	416	1450	3.7 volts, 180 Ah/kg actual cathode
C-Lithium-air	706	1600	2.5 volts, no weight added for catalyst or carbon
Lithium-LiMO ₂	971	2000	4 volts, 278 Ah/kg cathode, 3 x Li
Lithium-air	2050	2090	2.8 volts, 3xLi, no catalyst, carbon or solid electrolyte



Fig. 19. HEV powered by the Australian lead acid ultrabattery [65].

The numbers alone in Table 3 hardly justify the hype surrounding Li-O₂ cells based on storage capability alone. However, other considerations such as safety and cost might tip the scales; the full amount of the oxygen in these cells need not be held in as close a proximity to the anodes as in Li-ion cells, so thermal runaway might be minimized in solid electrolyte-based cells.

Lead acid batteries are getting a revival courtesy of the Australian CSIRO's invention of a hybrid carbon electrode. Known as the ultrabattery it is being used for both transportation and grid applications [65]. In the former, it has already passed over 100 000 mi in an HEV vehicle, as indicated in Fig. 19. For the latter, it is being evaluated for smoothing the power output from wind power at CSIRO. Both East Penn in the United States and Furukawa in Japan are developing the technology. It has the advantage of being lower cost than Ni/metal hydride.

Flow batteries have received much attention over the last 30+ years. They are readily scaled up, are most suitable for stationary grid-like applications, and potentially have low cost and so might get commercialized by the end of the decade.

There are some significant advantages of flow batteries that warrant more investment.

- 1) As the electrodes do not participate in the electrochemical reactions, they should be inherently more stable.

- 2) As the reactants are stored externally, the capacity and power capability can be designed independently.
- 3) Bipolar electrode technology can be used. No Li-ion batteries have been designed in a bipolar configuration because of concerns about electrolyte decomposition.

There are some challenges of flow batteries that will need overcoming.

- 1) The shunt currents, always present in bipolar flow systems, need minimizing.
- 2) Electrolyte issues include mixing of used electrolyte with fresh electrolyte in the storage tanks, and water and other species transferring across the membrane in the cell must be compensated for or removed from the storage systems.
- 3) All flow systems inherently have a low energy density, but probably higher than lead acid, which will limit their use to stationary applications.
- 4) Lower cost ion-exchange membranes need to be found.

Two systems in particular have received most attention: zinc–bromine and vanadium redox. Exxon initiated a zinc–bromine program in the mid-1970s using their bipolar plate fuel cell technology. They used an organic complexing agent to reduce the vapor pressure of bromine and increase safety, and used external tanks to hold the reactants, as shown in Fig. 20. The plates and cell components are mostly made out of plastic because bromine attacks most metals. The flowing electrolyte minimizes the formation of zinc dendrites, and the complexing agent reduces the solubility of bromine in the electrolyte and thus self-discharge. A continuing challenge to the use of bromine, and in the past chlorine, is the consequences of leakages. There are no commercial zinc–bromine batteries today.

In contrast, vanadium redox batteries have already found limited application, notably in Castle Rock, UT. This

facility opened in 2004 at a cost of \$1.3 million and operated for five years until a new substation was built; it stored 2 MWh of energy and could be discharged at 250 kW. In these batteries, at one electrode V^{5+} is reduced to V^{4+} and at the other electrode V^{2+} is oxidized to V^{3+} . Solutions of these redox couples are pumped by each side of an ion-exchange membrane in a bipolar electrode cell, as shown for the Zn/Br₂ cell. The large volume of electrolyte needed means that these systems have a low energy density. Although the battery appears to have been successful, its operator went out of business. It may well be that the A123 mobile trailer Li-ion grid systems are more cost effective, and having essentially no moving parts more reliable for remote or environmentally sensitive applications.

There is a need for flow systems using lower cost redox materials. Such a system, being funded by an ARPA-E contract, is the Cr–Fe couple. Here, CrCl₂ is the reducing component and FeCl₃ is the oxidizing component and a bipolar configuration is also likely here. Extensively studied in the 1980s, efforts by the National Aeronautics and Space Administration (NASA) and the Japanese were dropped without the construction of large batteries. It is also possible that some metal–air systems, like Zn–air, might be more feasible in flow format and there are efforts to design a Li-based flow system under ARPA-E funding. More details of flow batteries can be found in a 2006 review [66].

B. Where Will We Be in 25 Years?

It is important to remind the reader that energy storage devices, like batteries, capacitors, pumped hydro, or compressed air, do not obey Moore's law. There is an upper limit to their storage capabilities, and this can be readily calculated. As noted in the previous section, today we get less than 20% of the theoretical volumetric capacity out of a battery so there is room for improvement in the engineering of the system as well as in the use of new materials and reactions. If the desire is to get more energy out of a system at the same power rating, then flow batteries will be needed in which the tanks of the reactants are increased while keeping the electrochemical cell itself at the same size; in a similar way, a pumped hydro system is designed to provide output for a day rather than a few hours. Flywheels might be an exception to Moore's law, but even then there must be a limit to the speed at which the wheels can be spun.

In 25 years, oil availability will have peaked or at least the U.S. ability to obtain a disproportionate part of the world's supply will have peaked. The North American demand for energy will have to be reduced to that more typical of the world at large or alternative homegrown sources of energy will have to be used; today North Americans use twice as much energy per capita as Europeans. That is not sustainable in a world where China, India, and other developing countries want the same living

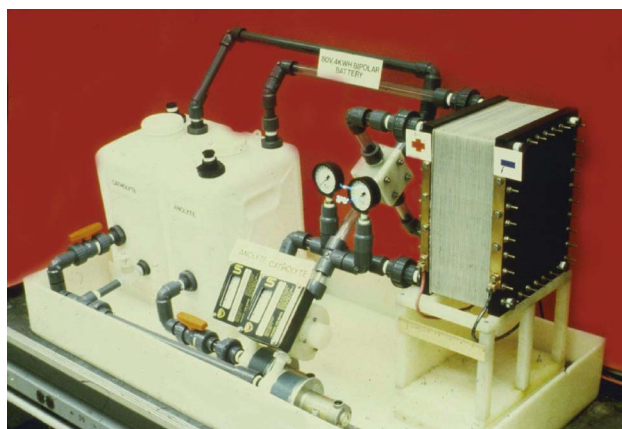


Fig. 20. Exxon laboratory zinc–bromine battery showing the bipolar electrochemical cell stack.

standards as the United States. The use of solar or wind will demand much more energy storage, probably at the local level as well as centrally. The United States will have a smart grid with price depending on demand, which again will push storage to the local level. This is not exactly revolutionary, as off-peaking heating of thermal storage media was popular at one period, and is likely to come back. This local level storage will also ameliorate against power outages, and give the individual more control over his life.

It is likely that simple low-cost flow systems will be built into every home, both thermal and electric. It is likely that all cars and other vehicles will be at least HEV, and probably PHEV with all-electric drive systems; they will also all contain thermal storage systems. In addition, the home, office, and vehicle electric and heat systems will be tightly computer integrated and their energy optimization will be tightly controlled using a price incentive.

In 25 years, the storage systems are likely to be sealed black boxes, using predominantly modular flow systems, that will be replaced in whole on failure. Low-cost sealed metal-oxygen or metal-sulfur will have advanced to gain a significant market share. Intercalation-based batteries will

retain a significant fraction of the market, but will have switched to nonlithium-based electrochemistry, as there is almost certainly not enough lithium in the world to provide for transportation, grid storage, and home/office storage. Replacing lithium will be magnesium, or if suitable electrodes can be found, sodium; zinc is not out of the question, but its storage capability is much lower because of the low cell voltage, ≤ 1.5 V, compared to the 4 V for lithium. For safety, it is likely that the sodium will be contained in some other host material, because the low melting point of sodium, around 100 °C, makes the possibility of thermal runaway too hazardous. Supercapacitors will have morphed into batteries, with the consumer having the opportunity to buy the desired battery that can supply electric energy from 90% power intensive to 90% energy intensive.

The final word on the degree of penetration of energy storage in the transportation and grid sectors will be political, but technology can win out if all else is equal. As we have all seen, visionary technology won out in the portable electronics area, and vision could lead to leap frog the present status to a completely new environmentally sensitive and cost-effective scenario in 25 years. ■

REFERENCES

- [1] S. Fletcher, *Bottled Lightening: Superbatteries, Electric Cars, and the New Lithium Economy*. New York: Hill and Wang, 2011.
- [2] K. H. LaCommare and J. H. Eto, *Understanding the Cost of Power Interruptions to U.S. Electricity Consumers*, 2004. [Online]. Available: <http://certs.lbl.gov/pdf/55718.pdf>
- [3] AES, *Laurel Mountain Wind Storage*, 2011. [Online]. Available: <http://www.aesenergystorage.com/projects.html>
- [4] NYPA, *Blenheim-Gilboa Pumped Storage Power Project*, 2010. [Online]. Available: <http://www.nypa.gov/facilities/blengil.htm>
- [5] TVA, *Raccoon Valley Pumped Hydro Facility*, 1978. [Online]. Available: <http://www.tva.gov/sites/raccoonmt.htm>
- [6] TVA, *Raccoon Mountain pdf Brochure*, 1978. [Online]. Available: <http://www.tva.gov/sites/pdf/raccoonmtn.pdf>
- [7] Dominion, *Bath County Hydro Storage*, 1985. [Online]. Available: <http://www.dom.com/about/stations/hydro/bath-county-pumped-storage-station.jsp>
- [8] *Dinorwig Power Station*, 1984. [Online]. Available: <http://www.fhc.co.uk/dinorwig.htm>
- [9] F. Crotogino, K.-U. Mohmeyer, and R. Scharf, *Huntorf CAES: More than 20 Years of Successful Operation*, 2001. [Online]. Available: http://www.uni-saarland.de/fak7/fze/AKE_Archiv/AKE2003H/AKE2003H_Vortraege/AKE2003H03c_Crotogino_ea_HuntorfCAES_CompressedAirEnergyStorage.pdf
- [10] PowerSouth, *Compressed Air Energy Storage*, 1991. [Online]. Available: http://www.powersouth.com/mcintosh_power_plant/compressed_air_energy
- [11] AES, *Energy Storage in Johnson City*, 2010. [Online]. Available: <http://www.aesenergystorage.com/projects/johnson-city-820-mw-operation.html>
- [12] Y. Y. Yao and J. T. Kummer, "Ion exchange properties of and rates of ionic diffusion in beta-alumina," *J. Inorganic Nuclear Chem.*, vol. 29, pp. 2453–2466, 1967.
- [13] M. S. Whittingham and R. A. Huggins, "Beta alumina—Prelude to a revolution in solid state electrochemistry," *NBS Special Publications*, vol. 364, pp. 139–154, 1972.
- [14] F. R. Gamble, J. H. Osiecki, M. Cais, R. Pishardy, F. J. Disalvo, and T. H. Geballe, "Intercalation complexes of Lewis bases and layered sulfides: A large class of new superconductors," *Science*, vol. 174, pp. 493–497, 1971.
- [15] M. S. Whittingham, "The role of ternary phases in cathode reactions," *J. Electrochem. Soc.*, vol. 123, pp. 315–320, 1976.
- [16] B. M. L. Rao, R. W. Francis, and H. A. Christopher, "Lithium-aluminum electrode," *J. Electrochem. Soc.*, vol. 124, pp. 1490–1492, 1977.
- [17] S. Flandois and B. Simon, "Carbon materials for lithium-ion rechargeable batteries," *Carbon*, vol. 37, pp. 165–180, 1999.
- [18] R. R. Chianelli, "Microscopic studies of transition metal chalcogenides," *J. Crystal Growth*, vol. 34, pp. 239–244, 1976.
- [19] M. S. Whittingham, "Lithium battery systems," *Electr. Veh. Expo.*, Adelaide, Australia, 1980.
- [20] J. R. Dahn, *Personal Communication Regarding MoliEnergy Batteries*, private communication, 2009.
- [21] W. Zhou, S. Upreti, and M. S. Whittingham, "Electrochemical performance of Al-Si-graphite composite as anode for lithium-ion batteries," *Electrochem. Commun.*, vol. 13, pp. 158–161, 2011.
- [22] SONY, *Nexelion Hybrid Lithium Ion Battery*, 2005. [Online]. Available: <http://www.sony.net/SonyInfo/News/Press/200502/05-006E/>
- [23] Q. Fan, P. J. Chupas, and M. S. Whittingham, "Characterization of amorphous and crystalline tin-cobalt anodes," *Electrochem. Solid State Lett.*, vol. 8, pp. A274–A278, 2007.
- [24] R. Zhang, S. Upreti, and M. S. Whittingham, "Tin-iron based nano-materials as anodes for Li-ion batteries," *J. Electrochem. Soc.*, vol. 158, pp. A1498–A1504, 2011.
- [25] X.-L. Wang, M. Feygenson, H. Chen, C.-H. Lin, W. Ku, J. Bai, M. C. Aronson, T. A. Tyson, and W.-Q. Han, "Nanospheres of a new intermetallic FeSn₅ phase: Synthesis, magnetic properties and anode performance in Li-ion batteries," *J. Amer. Chem. Soc.*, vol. 133, pp. 11 213–11 219, 2011.
- [26] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, "High-performance lithium battery anodes using silicon nanowires," *Nature Nanotechnol.*, vol. 3, pp. 31–35, 2008.
- [27] K. Mizushima, P. C. Jones, P. J. Wiseman, and J. B. Goodenough, "Li_xCoO₂ (0 < x ≤ 1): A new cathode material for batteries of high energy density," *Mater. Res. Bull.*, vol. 15, pp. 783–789, 1980.
- [28] J. B. Goodenough and K. Mizushima, "Electrochemical cell with new fast ion conductors," U.S. Patent 4 302 518, 1980.
- [29] J. B. Goodenough and K. Mizushima, "Electrochemical cell with few fast ion conductors," U.S. Patent 4 302 518, 1981.
- [30] M. S. Whittingham, "Chalcogenide battery," U.S. Patent 4 009 052 and U.K. Patent 1 468 416, 1973.
- [31] M. S. Whittingham, "Preparation of intercalated chalcogenides," U.S. Patent 4 040 017 and U.K. Patent 1 468 244, 1973.
- [32] Y. Nishi, "Performance of the first lithium ion battery and its process technology," in *Lithium Ion Batteries*, M. Wakihara and O. Yamamoto, Eds. Tokyo, Japan: Kodansha, 1998, pp. 181–198.
- [33] M. S. Whittingham, "Electrochemical energy storage: Batteries and capacitors," in *Fundamentals of Materials for Energy and*

- Environmental Sustainability*, D. S. Ginley and D. Cahen, Eds. Cambridge, MA: Cambridge Univ. Press, 2011, pp. 608–623.
- [34] T. Ohzuku and Y. Makimura, “Layered lithium insertion material of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for lithium-ion batteries,” *Chem. Lett.*, pp. 642–643, 2001.
- [35] Z. Lu, D. D. MacNeil, and J. R. Dahn, “Layered $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ cathode materials for lithium-ion batteries,” *Electrochem. Solid State Lett.*, vol. 4, pp. A200–A203, 2001.
- [36] I. Yonezu, H. Tarui, S. Yoshimura, S. Fujitani, and T. Nohma, “Development of new electrode materials for lithium ion batteries at SANYO,” in *Abstracts Int. Meeting Lithium Batteries*, 2004, vol. 12, p. 58.
- [37] M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek, and S. A. Hackney, “ Li_2MnO_3 -stabilized LiMO_2 ($M = \text{Mn}, \text{Ni}, \text{Co}$) electrodes for lithium-ion batteries,” *J. Mater. Chem.*, vol. 17, pp. 3112–3125, 2007.
- [38] Z. Li, N. A. Chernova, J. Feng, S. Upreti, F. Omenya, and M. S. Whittingham, “Stability and rate capability of Al substituted lithium-rich high-manganese content oxide materials for Li-ion batteries,” *J. Electrochem. Soc.*, vol. 159, pp. A116–A120, 2012.
- [39] A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, “Phospho-olivines as positive-electrode materials for rechargeable lithium batteries,” *J. Electrochem. Soc.*, vol. 144, pp. 1188–1194, 1997.
- [40] A123, *A123 Power Tools*, 2007. [Online]. Available: <http://www.a123systems.com/newsite/index.php/applications/cordless/>
- [41] BAESystems, *Hybrid Electric Buses*, 2011. [Online]. Available: <http://www.hybridrive.com/>
- [42] ElectricBus, *BA Staff Bus at Heathrow*, 2011. [Online]. Available: <http://www.valence.com/>
- [43] J. Chen and M. S. Whittingham, “Hydrothermal synthesis of lithium iron phosphate,” *Electrochem. Commun.*, vol. 8, pp. 855–858, 2006.
- [44] R. Malik, F. Zhou, and G. Ceder, “Kinetics of non-equilibrium lithium incorporation in LiFePO_4 ,” *Nature Mater.*, vol. 10, pp. 587–590, 2011.
- [45] A. F. Burke, “Electrochemical capacitors,” in *Linden’s Handbook of Batteries*, T. B. Reddy, Ed. New York: McGraw-Hill, 2011, pp. 39.31–39.44.
- [46] R. Kötz and M. Carlen, “Principles and applications of electrochemical capacitors,” *Electrochim. Acta*, vol. 45, pp. 2483–2498, 2000.
- [47] P. Simon and Y. Gogotsi, “Materials for periodical electrochemical capacitors,” *Nature Mater.*, vol. 7, pp. 845–854, 2008.
- [48] M. S. Whittingham, “Lithium batteries and cathode materials,” *Chem. Rev.*, vol. 104, pp. 4271–4301, 2004.
- [49] M. S. Whittingham, “Chemistry of intercalation compounds: Metal guests in chalcogenide hosts,” *Prog. Solid State Chem.*, vol. 12, pp. 41–99, 1978.
- [50] R. A. Huggins, *Advanced Batteries—Materials Science Aspects*. New York: Springer-Verlag, 2009.
- [51] *Basic Research Needs for Electrical Energy Storage*, U.S. Department of Energy, 2007.
- [52] G. G. Libowitz and M. S. Whittingham, *Materials Science in Energy Technology*. New York: Academic, 1979.
- [53] W. R. Grove, “Note sur une pile voltaïque d’une grande énergie,” *Comtes Rendus*, vol. 8, p. 497, 1839.
- [54] Y. Song, P. Y. Zavalij, and M. S. Whittingham, “ e-VOPO_4 : Electrochemical synthesis and enhanced cathode behavior,” *J. Electrochem. Soc.*, vol. 152, pp. A721–A728, 2005.
- [55] G. Hautier, A. Jain, S. P. Ong, B. Kang, C. Moore, R. Doe, and G. Ceder, “Phosphates as lithium-ion battery cathodes: An evaluation based on high-throughput ab initio calculations,” *Chem. Mater.*, vol. 23, pp. 3495–3508, 2011.
- [56] W. Zhou, S. Upreti, N. A. Chernova, G. Hautier, G. Ceder, and M. S. Whittingham, “Iron and manganese pyrophosphates as cathodes for lithium ion batteries,” *Chem. Mater.*, vol. 23, pp. 293–300, 2011.
- [57] F. Wang, R. Robert, N. A. Chernova, N. Pereira, F. Omenya, F. Badway, X. Hua, M. Ruotolo, R. Zhang, L. Wu, V. Volkov, D. Su, B. Key, M. S. Whittingham, C. P. Grey, G. G. Amatucci, Y. Zhu, and J. Graetz, “Conversion reaction mechanisms in lithium ion batteries: Study of the binary metal fluoride electrodes,” *J. Amer. Chem. Soc.*, vol. 133, pp. 18 828–18 836, 2011.
- [58] SionPower, *Lithium Sulfur Batteries*, 2012. [Online]. Available: <http://www.sionpower.com/>
- [59] K. M. Abraham and Z. Jiang, “A polymer electrolyte-based rechargeable lithium/oxygen battery,” *J. Electrochem. Soc.*, vol. 143, pp. 1–5, 1996.
- [60] B. D. McCloskey, D. S. Bethune, R. M. Shelby, G. Girishkumar, and A. C. Luntz, “Solvents’ critical role in nonaqueous lithium,” *J. Phys. Chem. Lett.*, vol. 2, pp. 1161–1166, 2011.
- [61] T. Ogasawara, A. Débart, M. Holzapel, P. Novák, and P. G. Bruce, “Rechargeable Li_2O_2 electrode for lithium batteries,” *J. Amer. Chem. Soc.*, vol. 128, pp. 1390–1393, 2006.
- [62] B. D. McCloskey, R. Scheffler, A. Speidel, D. S. Bethune, and A. C. Luntz, “On the efficacy of electrocatalysis in non-aqueous Li-O_2 batteries,” *J. Amer. Chem. Soc.*, vol. 133, pp. 18 038–18 041, 2011.
- [63] Polyplus, *Polyplus Lithium Air and Sea Water Cells*, 2012. [Online]. Available: <http://www.polyplus.com/liair.html>
- [64] Gigaom, *Rechargeable Lithium Oxygen Batteries*, 2011. [Online]. Available: <http://gigaom.com/>
- [65] CSIRO, *Ultra Battery*, 2008. [Online]. Available: <http://www.csiro.au/Portals/Media/UltraBattery4HybridCars.aspx>
- [66] C. P. de León, A. Frías-Ferrer, J. González-García, D. A. Szánto, and F. C. Walsh, “Redox flow cells for energy conversion,” *J. Power Sources*, vol. 160, pp. 716–732, 2006.

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