

Batteries for Vehicular Applications

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Abstract. This paper will describe battery technology as it relates to use in vehicular applications, including hybrid-electric vehicles (HEV), electric vehicles (EV), and plug-in-hybrid-electric vehicles (PHEV). The present status of rechargeable batteries, the requirements for each application, and the scientific stumbling blocks that stop batteries from being commercialized for these applications will be discussed. Focus will be on the class of batteries referred to as lithium batteries and the various chemistries that are the most promising for these applications. While Li-ion is expected in HEVs in the very near future, use in PHEVs are expected to be more gradual and dependent on solving the life, safety, and cost challenges. Finally, batteries for EVs remain problematic because of the range and charging-time issues.

INTRODUCTION TO BATTERIES

Several electrical energy storage and conversion devices have been considered for use in vehicle applications. These are illustrated in Figure 1 in the form of a Ragone plot, wherein the abscissa is specific power (which can be thought of as acceleration in a vehicle) and the ordinate is specific energy (or range in an EV). The graph shows these quantities for various batteries, electrochemical capacitors, and fuel cells. Note that this plot shows specific energy and power on a cell level for batteries made for many different applications, from consumer electronic to vehicles. An additional derating will need to be applied when analysis is done on the pack level. The figure shows that lithium-ion (Li-ion) batteries are superior to nickel metal hydride (Ni-MH) batteries for all three applications from a performance standpoint. The figure also shows that no battery system has the ability to provide energy close to what is possible with gasoline (Internal combustion, or IC-Engine). Finally, the figure suggests that batteries are superior to capacitors for applications where the time of discharge is greater than the order of seconds.

The United States Advanced Battery Consortium (USABC) has set the requirements needed for batteries to be used in EV, PHEV, and HEV application.¹ These requirements cover a wide range of issues and include energy and power. In order to compare the requirements to the performance of these devices illustrated in Figure 1, a few assumptions have to be made, which are done here for the sake of

simplicity. While the USABC requirements for power represent a peak power for a 10s charge/discharge, the systems in Figure 1 show average power. Similarly, the USABC requirements show energy as an *available* energy, which typically is less than the total energy of the cell. For a HEV, available energy can be as little as 20-30% of the total energy, while for an EV or PHEV, this could be as large as 70-80%.

Despite these differences, a superposition of the USABC requirements onto Figure 1 is illustrative. The figure shows that while Li-ion batteries can easily satisfy HEV requirements, the energy is much smaller than the requirements for EVs. Similarly, the energy needs of a 40 mile PHEV (96 Wh/kg available energy) could be achieved by a high-energy Li-ion cell (similar to the batteries used in the Tesla Roadster).^a

However, while the plot captures the performance map of various batteries, other criteria need to be considered, including cost, cycle and calendar life, and safety. Moreover, these factors are connected to each other. For example, while PHEVs *appear* possible with Li-ion batteries today from an energy standpoint, this would require the use of batteries that are not made for EV applications and that are cycled over a very wide state of charge (SOC) range, thereby limiting cycle life. One could increase the life by limiting the extent to which these batteries are charged, however, this would limit the energy of the cell, and thereby increase the cost, and the volume and weight of the final battery. Indeed, an analysis of presently-available EV batteries with characteristics that enhance cycle/calendar life suggests that meeting the energy requirements for a 40 mile PHEV is difficult. Finally, the importance of each of these factors changes from application to application. Therefore, while peak power could be an important criterion for a HEV, energy density would be a critical parameter in an EV. Some criteria, like cost and safety, remain challenges in all applications.

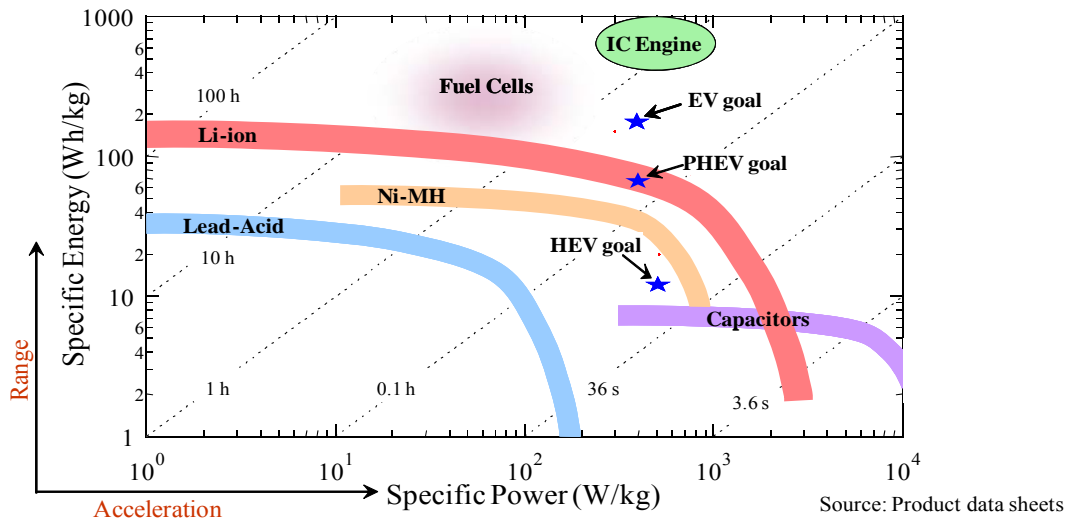


FIGURE 1. Ragone plot (specific power density in W/kg vs. specific energy density in Wh/kg) of various electrochemical energy storage and conversion devices.

^a Assuming a packaging factor of 0.7, a consumer electronics battery with energy of 180 Wh/kg has a pack-level energy density of 126 Wh/kg. A 76% SOC range of cycling results in this battery meeting the requirements. However, note that typical EV batteries have a much lower energy density (pack level of 110 Wh/kg) due to the life requirements.

While complicated, the interplay between these various factors is tractable and suggests that Li-ion batteries remain the most promising candidate for use in vehicular applications. The three main reasons for this conclusion are the higher energy, higher power, and the potential for lower cost of Li-ion batteries when compared to Ni-MH batteries. This conclusion has been the reason why significant research efforts have been directed toward Li-ion batteries. In this paper, we will explore the limitations that Li-ion batteries face when used in each of the three applications (HEV, EV, and PHEV), the underlying technical challenges behind the limitations, and the approach taken by researchers the world over to address these limitations. We begin with a brief tutorial on batteries.

Batteries typically consist of two electrodes, an anode and a cathode with a separator between them to prevent shorting. The cell is filled with electrolyte. Figure 2 illustrates a typical Li-ion cell sandwich consisting of a graphite anode and a lithium cobalt oxide cathode (LiCoO_2).

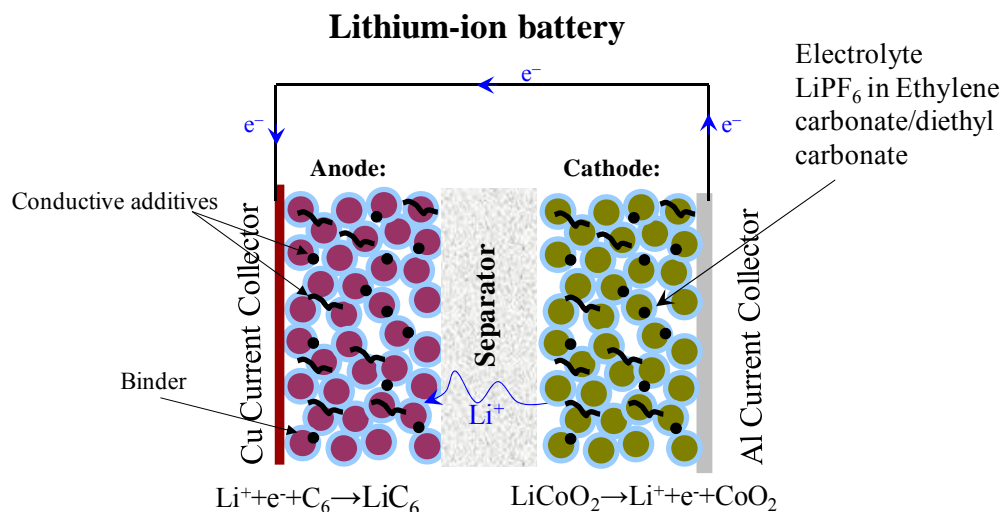


FIGURE 2. Schematic of a typical Li-ion cell.

The electrodes consist of active materials bound together with an electronically insulating binder and conductive additives. Each electrode is pasted onto current collectors. During charge, Li is removed from the cathode (or positive electrode), transferred through the separator *via* the electrolyte and is inserted into the anode. The reverse occurs on discharge. The difference in voltage of the cathode and the voltage of the anode is the cell voltage. The amount of Li that is stored in each of these materials is related to the capacity (often given in mAh/g). The product of the voltage and the capacity is the energy. How quickly the Li is transferred from one electrode to the other (or how quickly the energy is removed) is related to the power. More details on batteries can be found in references 2, 3, 4, and 5.

Figure 3 shows the typical steady-state charge of the anode and cathode of a Li-ion cell with a graphite anode and a LiCoO_2 cathode in an organic electrolyte consisting of a Li salt (lithium hexafluoro phosphate, LiPF_6) in a solvent (*e.g.*, ethylene carbonate

and diethyl carbonate). This is the battery used in laptops and cell phones. The voltage of each electrode is represented with respect to a Li-metal reference electrode. As the Li is removed from the cathode, its potential increases, while the potential of the anode decreases with insertion of Li. The process of Li moving in and out of the electrodes is referred to as intercalation/deintercalation. The voltage of the battery is the difference in voltage of the cathode and the anode, which increases as charge proceeds. The abscissa represents how much Li is stored in the cell, while the ordinate shows at what voltage the Li is inserted/removed from the materials. In order to increase the energy of the battery three avenues can be pursued, namely (i) increase the voltage of the cathode, (ii) decrease the voltage of the anode, and (iii) increase the capacity of the cell. However, the thermodynamics of electrochemical reactions other than the intercalation of Li (referred to as side reactions) limit these quantities.

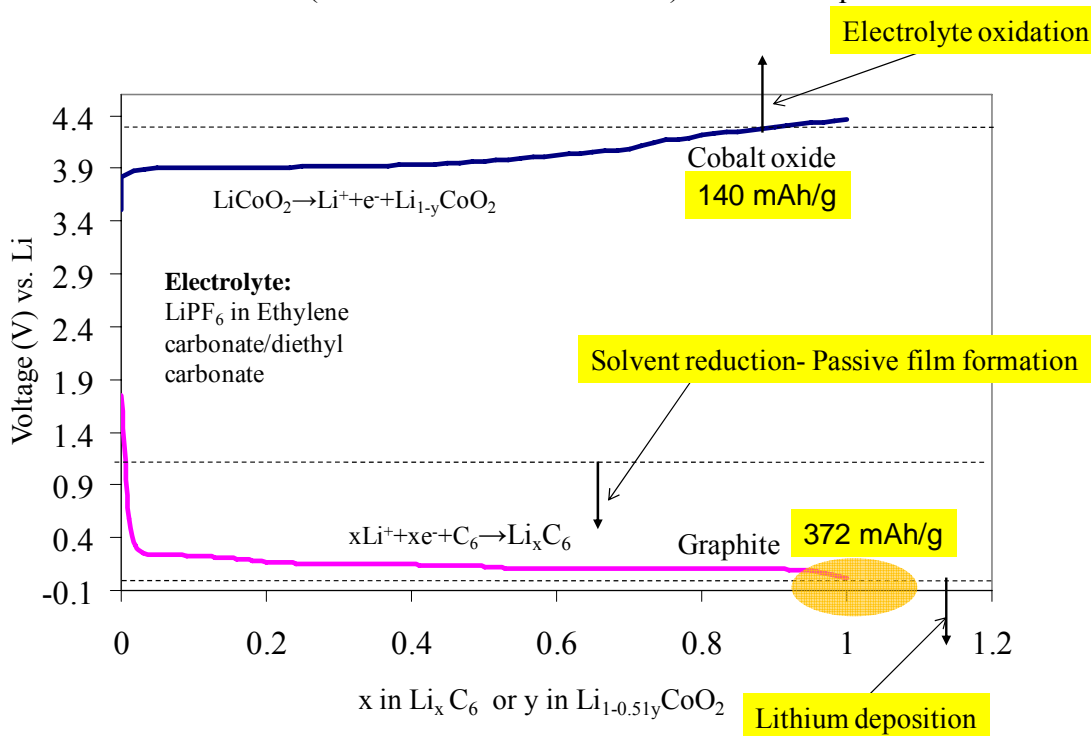


FIGURE 3. Steady state charge curve of a Li-ion cell consisting of a graphite anode and a LiCoO₂ cathode. The graph shows the half cell potentials and the thermodynamics potentials for various side reactions.

The three side reactions worth mentioning in this plot are the oxidation of the solvent that occurs above ~ 4.2 V vs. Li, Li-metal deposition that occurs below 0.0 V vs. Li, and solvent reduction that occurs below ~ 1 V vs. Li. These three reactions not only limit the energy of the cell, they are also implicated in the life and safety problems associated with Li-ion batteries. Staying within the voltage window allows these problems to be minimized, at the loss of energy. The tradeoffs that are needed to balance these various parameters are captured by Figure 3.

Innovation in Li-ion batteries can occur in two ways, (i) *via* engineering advances that reduce, *e.g.*, the thickness of the separator and/or (ii) *via* innovation in the materials used as the active material. For example, the chemistry used in present-day

cell phone and laptop batteries ($\text{LiCoO}_2/\text{graphite}$) has a theoretical energy density of ~ 360 Wh/kg (this accounts for only the weight of the active material and not the weights of the other components in the cell such as the current collectors, electrolyte, binders, and cell packaging). The practical energy density of a packaged 18650 cell is ~ 190 Wh/kg. Fifteen years ago, in the early days of Li-ion, this number was ~ 90 Wh/kg, using the same material sets.⁶ In other words, over the last 15 years, engineering advances have resulted in a doubling of the energy density of Li-ion batteries. It is expected that in the future, improvements in performance will occur by moving to new higher energy materials.

Fortunately, it has been observed that Li can intercalate into many different anode and cathode materials. At present, three classes of cathodes, four classes of anodes, and four classes of electrolytes are being considered for use in Li-ion cells. Depending on the combination of the anode, cathode, and electrolyte, one can have a completely new battery with changes to the energy, power, life, safety characteristics, low temperature performance, *etc.* These classes are illustrated in Figure 4 for the three components of the battery.

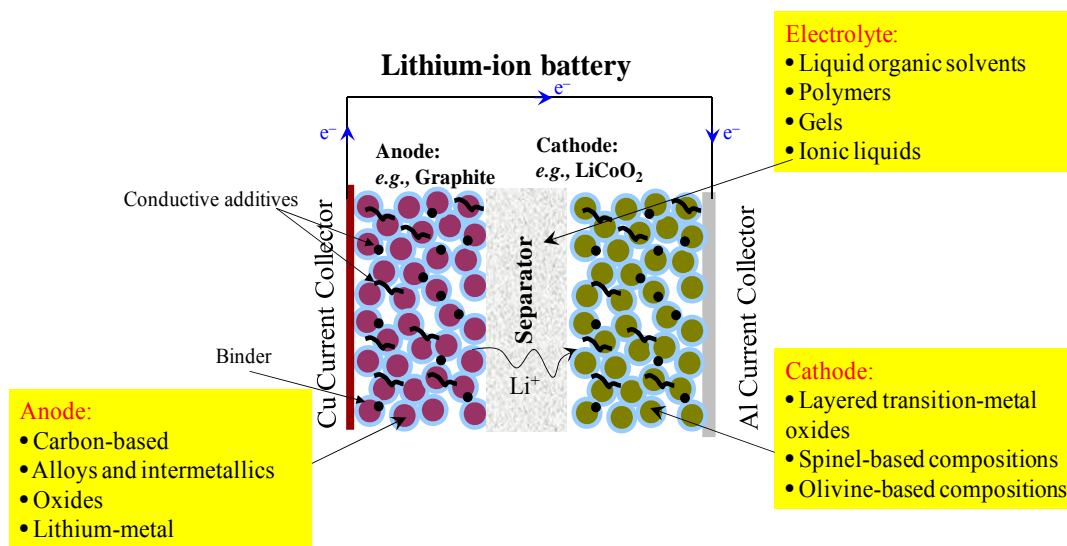


FIGURE 4. Schematic of a Li-ion cell with the various anode, cathode, and electrolytes that are presently being considered. Changing the combination results in changes to the energy, power, safety, life, and cost.

Each of these classes is a collection of numerous specific materials with their own different characteristics. For example, the LiCoO_2 electrode used today falls under the class of layered materials. Its capacity is 140 mAh/g. A new cathode emerging in the market is $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), also a layered material but with a capacity of 185 mAh/g. This increase in capacity means a significant increase in the energy of the cell, reiterating that many different materials combinations can be used to tune the battery to suit the application for which it is used. This behavior of Li batteries makes it very different from other classes of batteries, for example, the lead-acid system where the material set is fixed. It also adds additional degrees of freedom for researchers to find new materials and in effect make a new battery.

One issue worth mentioning is the concept of capacity balancing. Today's Li-ion batteries are typically referred to as cathode limited. In other words, the capacity of the cathode (140 mAh/g for LiCoO₂) limits the capacity of the battery, as it is smaller than the capacity of the anode (372 mAh/g for graphite). What this means is that the cathode has a significantly higher impact compared to the anode in increasing the energy of the cell. A quick calculation shows that an order of magnitude increase in the anode capacity increases the capacity of the cell by only 35% (one would also need to see at what voltage this new anode operates in order to estimate the improvement in energy).

While the flexibility of Li batteries provides the means to tune the battery's characteristics, it appears that no ideal combination has been found that satisfies the needs of vehicular applications. We now briefly look at the three applications, the status of batteries in these applications, and the research that is being pursued.

BATTERIES FOR HEVs

Over the last 5 years enormous progress has been made in using Li-ion batteries for HEV applications. The most studied system typically consists of the NCA cathode with a graphite anode. With continuous improvements this system has overcome many of the limitations and has come closer to satisfying a majority of the requirements set out by the USABC. In particular, the calendar life of this chemistry has been projected to be greater than 15 years based on accelerated testing, when the SOC of the battery is controlled carefully. This promising development provides hope for use in vehicles.

Despite these advances, three main barriers remain before commercialization: (i) cost, (ii) low-temperature operation and (iii) safety.⁷ It has been shown that a large proportion of the cost of HEV batteries is due to the separator (25%) and the electrolyte (17%) (note that in a HEV cell, where the electrodes are thin, there is more separator area for the same size compared to an EV battery).⁸ Therefore, efforts to make low-cost separators would help with the cost reduction in the cell. An ability to make low-cost separators thinner, without compromising safety, would enhance power, and minimize cost simultaneously. In addition, lower cost electrolytes and cathodes would also help in decreasing the cost of the battery. Finally, as the important metric for a HEV is \$/kW of power, a new chemistry that promises higher power at the same cost per cell would result in a lower pack cost.

When operating Li-ion batteries at low temperatures (less than 0°C), it has been seen that the power capability decreases significantly because of increased resistance in the cell. It is thought that the increased resistance is caused by the reduction in the kinetic rate constants of the electrochemical charge-transfer reaction.⁹ This has implications during regeneration where the anode in the Li-ion cell is accepting Li at high rates. It has been observed that instead of intercalating into the graphite structure, the Li plates on the surface. The Li metal then reacts with the electrolyte and gets consumed, leading to capacity fade. While it is known that the choice of the solvent can have a significant impact on the low-temperature performance, these special solvents come at an additional cost. An alternative technique is to use an anode that allows the lowering of the impedance without causing Li plating. This can

be achieved if the voltage of the anode is much higher than the voltage for Li-plating, allowing a bigger window before plating occurs. Lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is a candidate that allows this feature because its voltage is 1.5 V vs. Li. Companies such as Toshiba, Enerdel, and Altair Nano are pursuing this concept to allow low-temperature operation and fast-charge capability (in addition to possible safety and life enhancements). However, the high anode voltage results in a low cell voltage and therefore decreases the energy of the battery.

It also should be noted that if the HEV is designed so that the battery is not used when cold but instead is allowed to warm up using the IC engine, then the problem of low-temperature operation could be circumvented. At present, it appears that the HEVs of the near future will be using this strategy. A pure EV would be prone to have a problem from this low-temperature limitation because no means exist to heat the battery when it is not plugged into an electrical outlet. Here, again, the problem could be solved by not allowing regeneration until the battery warms, and by using the battery to power the car (albeit at lower acceleration) until it self-heats.

The last limitation of Li-ion batteries is the safety of the pack, highlighted by the recent incidents involving fires of consumer-electronics batteries. The main cause of safety limitations in Li-ion cells can be characterized by the three stages in which thermal runaway occurs.¹⁰ In stage 1, an unexpected failure occurs in the cell, *e.g.*, internal shorting (*e.g.*, due to metal particles) or malfunction of the overcharge protection system. This results in the temperature of the cell increasing to around 125°C, where a reaction that involves decomposition of a passive layer on the anode (called the solid electrolyte interphase layer or SEI) occurs; an exothermic reaction that increases the temperature further. As the temperature increases to above 180°C, in some cathodes, the oxygen from the lattice is released, resulting in a rapid increase in heat in a short time. This chain reaction results in the smoke and the fires that have been observed in Li batteries.

One can prevent/retard these reactions in different ways. For example, using a cathode that does not release oxygen could help in suppressing the final exothermic step. Lithium iron phosphate is one such cathode that is being pursued by various companies, notably, A123 systems and Phostech. A second approach is to prevent the cell from approaching these temperatures by preventing the decomposition of the SEI. Lithium titanate is an example of an anode where no SEI forms and so it has been argued that this makes the battery safer. Finally, research efforts are underway to develop overcharge protection mechanisms, such as redox shuttles, electroactive polymers, and high puncture-strength separators to prevent internal short circuits. These ideas are aimed at preventing the cell from reaching the temperatures where the anode reactions occur. Finally, electrolytes that are not flammable and nonvolatile (*e.g.*, ionic liquids) help minimize the impact of these incidents even if the reactions do occur.

To summarize, three problems prevent the widespread commercialization of Li-ion batteries for HEVs today, cost, low-temperature operation, and safety. However, in the short-term, various engineering solutions can be adopted that can prevent the latter two. With cost being a highly socio-economic factor, it is thought that HEVs with Li-ion will start reaching the marketplace within the next few years.

BATTERIES FOR EVs

We will now examine the use of Li-ion batteries for EV applications. As was pointed out previously, Figure 1 suggests that the energy density of Li-ion batteries is not sufficient for use in present-day cars to provide the necessary range to make them commercially viable. A typical rule-of-thumb is that a sedan can go 1 mile on 300 Wh of battery. In other words, a car with 300 mile range requires a 90 kWh pack that can fit in the vehicle with little impact to passenger and luggage space. Presently available EV batteries have a specific energy of ~ 110 Wh/kg and 160 Wh/l,¹¹ suggesting that the 90 kWh battery will weigh 1800 lbs and have a volume of 148 gallons; far too large for existing vehicles. These energy numbers are on a pack level and are therefore smaller than those on a cell level. Further, note that these numbers are not meant to be precise, rather they are estimates to illustrate the challenges.

Arguments could be made that one may not need a 300-mile-range vehicle, that one could drive more than 1 mile with 300 Wh (for example, *via* the use of lightweight materials and better body design), and that one could enhance the specific energy on the pack level using lightweight battery packaging.^b All these would help make EVs a reality. However, the cost of such a vehicle would still remain large, and, arguably, prohibitive. For example, the battery pack in the Tesla Roadster is reported to be \$25,000. The fact that the Tesla batteries are made for consumer electronic applications, where the cost of batteries is considerably lower than that for vehicles, highlights the magnitude of the problem. Similar to HEVs, the important quantity is the \$/kWh of the battery (a more comprehensive metric would be \$/kWh/year or a lifetime cost on an energy basis^c). Therefore, a higher energy chemistry could be a route to decreasing the cost of these batteries. Three ideas that are being pursued are discussed here.

As pointed out before, the capacity of cathodes used in consumer electronic batteries are limited by the solvent oxidation reaction that occurs at ~ 4.2 V *vs.* Li. At these limits, only $\sim 50\%$ of the lithium is removed from the lattice of the cathode. Tremendous improvements could be made if the extra lithium can be accessed. Efforts are underway to find new electrolytes that can be used in high-voltage cathodes. However, as of today, there appears to be no electrolyte that shows promise in increasing the voltage significantly. An interesting recent advancement has been in altering the surface of the cathode in order to modify the interface where reaction occurs. For example, it has been shown that coating the cathode with a layer of aluminum phosphate (AlPO_4)¹² allows the potential to be pushed to higher values, thereby increasing the capacity and the energy, with little loss in capacity. This modification of the interface allows us to think of new ways to enhance the energy of the cell while maintaining cycle life and safety.

The second possibility is to change the anode to enhance the energy of the cell. Two options are being pursued in this area, (i) the use of anodes that alloy with Li, such as silicon and (ii) the use of Li metal. In area one, anodes, such have silicon, are

^b One can perform an optimistic calculation using a high-energy Li-ion cell of say 180 Wh/kg specific energy with a packaging factor of 0.8 resulting in a pack level specific energy of 144 Wh/kg. For a 200 mile vehicle, this would require 900 lbs of battery; a more manageable number.

^c For a Tesla battery, which is a 56 kWh battery which would last, as reported, 5 years, the \$/kWh/year is 90. The USABC long-term goal is \$10/kWh/year (and 15 for the short-term) for EVs.

attractive because they have high capacity (~3700 mAh/g) when compared to graphite (372 mAh/g).¹³ Despite having a higher voltage compared to graphite (0.5 V vs. 0.1 V), the use of Si results in an increase in energy density by ~25-35%. However, several problems prevent alloys from being commercialized including a large volume change (~270% for silicon) with cycling that results in particle cracking/isolation, a large 1st cycle loss in capacity that results in Li being consumed to make a passive layer and not being active to provide capacity, and a continuous consumption of Li from cycle to cycle that limits the cycle life.¹⁴ Several approaches are being pursued to alleviate these limitations.

Two that are worth noting are the use of what is termed “active-inactive matrix” where the active component (Si or Sn) is embedded in an inactive matrix (*e.g.*, carbon),¹⁵ and the use of novel structures to accommodate the volume change. In the first approach, the carbon allows the expansion of the alloy without particle cracking. However, the added weight and volume of the inactive component limits the capacity of these anodes to ~1200 mAh/g. This concept is used in the Nexilion cell introduced by Sony Corporation. In the second concept approach, micron-sized silicon pillars that reversibly cycle with high capacity are used.¹⁶ A nano-sized analog of this concept was recently reported by a group at Stanford University.¹⁷ While interesting, these structures require expensive and slow processing.

While these two approaches show promise in accommodating the volume change, efforts need to be made to reduce the 1st cycle capacity loss (which scales with surface area) and the cycle-to-cycle loss of Li. Use of “*in situ* SEI-formers” like the SLMP powder marketed by FMC Corporation could help with the former.¹⁸ The use of additives could help with the latter.

In area two, using Li metal as the anode brings the promise of a large capacity (3800 mAh/g) at a voltage of 0.0 V, thereby increasing the energy of the cell. Lithium metal has been used in primary Li batteries for decades, however, its use in secondary batteries have not been successful because of problems during charging. During charge, Li plates on the anode and, similar to plating of other metals like zinc, does not plate uniformly. Instead, dendrites of Li grow on the surface and, with time, penetrate the separator and short the cathode. In addition, dendrites break and isolate Li resulting in capacity fade.

There have been numerous efforts over the decade to stop the dendrites from growing by placing the anode against a hard surface, such as a solid polymer electrolyte. It has been hypothesized that the hard surface of the polymer would prevent the dendrites from penetrating. However, it has been observed that as the stiffness of the polymer increases, its conductivity decreases, thereby limiting the power capability of the cell. This interplay between conductivity and stiffness has resulted in the inability to effectively prevent dendrites. The use of block copolymers, where one block is made of a stiff material like polystyrene, and the second block is made of a conducting phase, like polyethylene oxide, has allowed the decoupling of conductivity and stiffness.¹⁹ However, as of today, these polymers operate at 80 C and have significantly lower conductivity compared to liquid electrolytes. The use of polymers for Li batteries is being pursued by companies such as Sion Power and Seeo Inc.

Another concept is the use of single-ion conducting glasses to isolate the Li. This concept has been explored by Polyplus Battery Company where it has been shown that the Li can be completely isolated to the point where it can be dipped in water. This concept is intriguing in that it enables the development of very high energy cells like Li-air and Li-sulfur. These glasses are not very conductive and are prone to defect formation. Advances in the behavior of solid polymers and ionic glasses could provide huge benefits in batteries.

While these approaches provide a pathway for enabling a higher energy cell that could allow the development of EVs, they fail to solve one other problem, namely, charging time. With typical battery charge times ranging from 3-8 hours, a change in lifestyle is needed when compared to using a gasoline car. While fast-charge batteries do exist (*e.g.*, Altair Nano and Toshiba), these come at the expense of energy. Further, infrastructure questions arise concerning the ability of the grid to handle a pure electricity-based transportation economy with fast-charge batteries. The issues of range and charging are circumvented with the use of a PHEV.

BATTERIES FOR PHEVs

The PHEV is an ideal compromise between the minimal fuel-saving advantage of the HEV and the range/charging-time issue of the EV. With the addition of the internal combustion engine for longer trips and a large battery pack to sustain 10-40 miles of equivalent electric range, the PHEV captures the best of both concepts. As suggested previously, the energy of the Li-ion cell is connected with the life and enhancing one typically lessens the other. While high energy Li-ion cells, similar to ones used in consumer electronic applications, could probably satisfy the range requirements for a 40 mile PHEV, the ability of these batteries to last 15 years is highly questionable. Typical EV batteries today do not appear to possess the energy needed for a 40 mile range. However, recent reports suggest that battery manufacturers are increasing moving to lightweight packaging that should allow the specific energy to increase. In addition, presently-available batteries should be sufficient to satisfy the energy requirements of PHEVs that have a lesser EV range (*e.g.*, 20 miles). However, two problems still need addressing, namely, cost, and cycle/calendar life.

Present cost estimates suggest that a 40-mile PHEV battery can cost upwards of \$10,000.^d While battery companies have been reporting cycle life of Li-ion cells in the 3000-5000 cycle range (approaching the USABC requirements), the more important question is the calendar life of these cells, particularly because these

^d USABC goal for available energy of a PHEV-40 is 11.6 kWh. Assuming a 70% range, this means that the total battery size would be 16.5 kWh. Assuming a cost of \$1000/kWh for a PHEV cell, this would mean a total cost of \$16,500 for the battery pack. While not well understood, the life of this battery *could* be 10-15 years. One could perform an alternate calculation: Assuming that one uses a consumer electronic battery with the same characteristics as the battery for a Tesla Roadster, a 40 mile PHEV would cost \$5,000 (1/5th the cost of the Tesla battery of total energy 11.2 kWh). Assuming, optimistically, that this battery lasts 5 years, this means a yearly cost of \$1000 for the battery pack. Assuming that the battery is cycled 300 times in a year (for a total of 12,000 miles pure EV driving), the cost of electricity would be \$270 at \$0.08 per kWh. In other words, one would need \$1270 per year to pay for the battery and the electricity per year. Assuming a 3 year battery life (arguably more realistic) increases this cost to \$1935 per year. To drive the same miles in a gasoline car with 30 mpg mileage would require \$1800 per year, assuming gasoline costs at \$4.5 per gallon (costs in the San Francisco Bay Area as of June 2008). Both calculations allude to the need for creative financing options (*e.g.*, battery leasing) to offset the initial investment needed to buy a PHEV.

batteries may spend a considerable part of the time at high SOCs, the state where Li-ion batteries are most prone to exhibit capacity fade. Strategies are being pursued that involve decreasing the maximum SOC of the battery in order to enhance the life; however, these come at the expense of energy and therefore increase the cost of the pack. As of today, no clear data exists that shows the ability of Li-ion batteries to sustain 15 year life under PHEV conditions. This is expected to become available in the near future.

Concepts that involve increasing the energy of the battery *via* new materials, described in the EV section, will prove to be very effective in decreasing the cost (by decreasing the \$/kWh). In addition, careful use of additives/coatings to modify the electrode/electrolyte interface in order to retard side reactions in the cell can help to enhance the life of the battery, without sacrificing energy. Finally, new materials that show inherent stability could also be useful in improving the life of these batteries.

We end the discussion of PHEVs by reminding the reader that safety remains a concern for all three applications and that the ideas to enhance safety suggested in the HEV section are applicable for PHEVs (and EVs).

FUTURE OF BATTERIES

The energy density of batteries has been increasing at the rate of ~5% per year over the last 15 years, well below the improvements that have been made in semiconductor devices (*e.g.*, Moore's law). The question arises as to how batteries will improve over the next 15 years. While difficult to predict, one can look at advances in the literature and project the impact these advances would have on energy. We choose to look at specific energy, although energy density is also important. This is summarized in Figure 5 where the specific energy is captured at the cell level. We split the plot into "low risk" where two advances are expected. One involves the move to a NCA-like cathode from LiCoO₂ (which is already underway) and the second involves the move to an active-inactive alloy (similar to the Nexilion cells, but with higher capacity). We then describe higher risk systems that involve moving to high-voltage-transition-metal-oxide (TMO) cathodes and to alloy anodes that have much larger capacity. These are considered possible, if the concept of coatings work to enhance the capacity of cathodes without compromising safety and life and if alloys, like Si, prove to meet the cycle life requirements. While both these are far from certain, the literature results are encouraging.^{12,20} Because of the uncertainty, we denote this as higher risk. These advances, if successful, would result in the doubling of the energy of present day batteries; a significant increase.

Next, we address the issue of the theoretical limit of the energy of batteries. While some use a periodic table to evaluate this number, we choose to highlight systems that are very far from reality, but have been alluded to in the literature. Three of these systems are listed in Figure 6 including zinc-air, lithium-sulfur and lithium-air. Note that the numbers in this figure are theoretical energies (that do not include any weights except that of the active material). The figure shows that batteries today are very far from achieving the theoretically maximum-possible energy. Efforts are underway both in the research community and in industry to examine these systems. For example, the Zinc-air technology is being pursued by ReVolt Technologies in Sweden

and the Li-S cell is the focus of Sion Power. However, note that while the figure shows the theoretical specific energy, practical values are far below these quantities. For example, the target for Li-S cells is in the range of 350 Wh/kg; less than a doubling of presently-available systems. This shows the difficulty involved with these chemistries and the long-term nature of the research for them to be commercial.

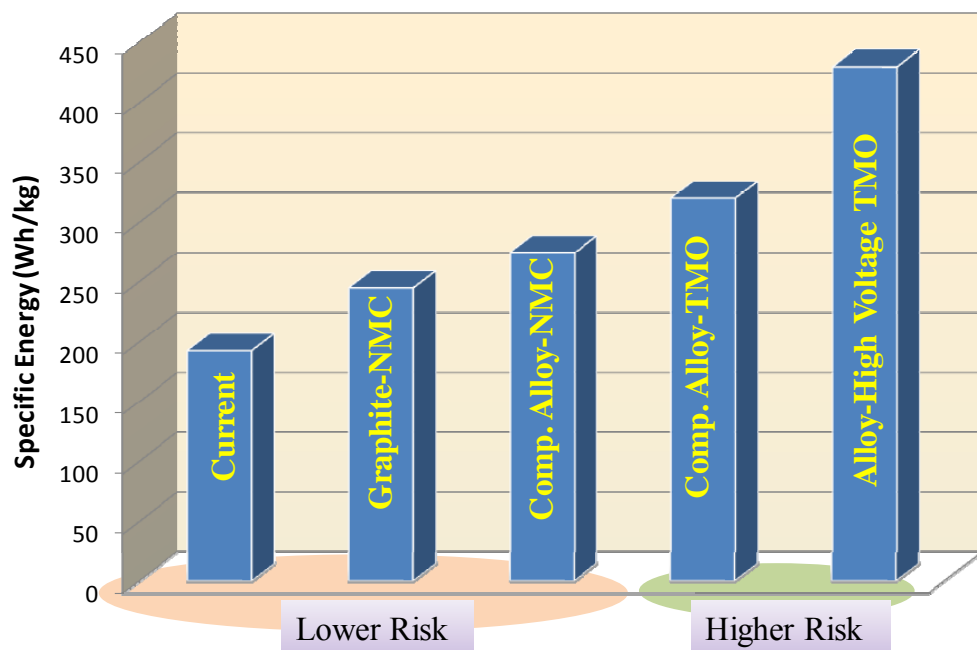


FIGURE 5. Projected increase in energy density (Wh/kg) of Li-ion cells on a cell level; NMC - $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, TMO - transition metal oxide. Based on Draft of FreedomCAR PHEV R&D Plan: http://www1.eere.energy.gov/vehiclesandfuels/features/phev_plan.html

Finally, we examine the need for non-Li-based systems for energy storage for vehicles. While systems are being researched (like magnesium and sodium), these appear further away from commercialization. Considering the wide variety of materials that Li can intercalate into, it appears that Li-based batteries (whether Li-ion or Li-metal) offer many opportunities for improvements that are worth pursuing. While it can be argued that being dependent on a single cathode or anode material (like being dependent on platinum in a fuel cell) would lead to resource limitations, one should note that with the wide material set for the anode and cathode for use in a Li-ion cell, one has opportunities to spread the risk among many different metals. The one common metal that is needed for all Li-based cells is Li. Back of the envelope calculations show that Li-metal limitations should not be an issue for at least the short to intermediate term. However, a comprehensive study is probably needed to ensure that this resource is not limited if widespread penetration of PHEVs and EV do occur.

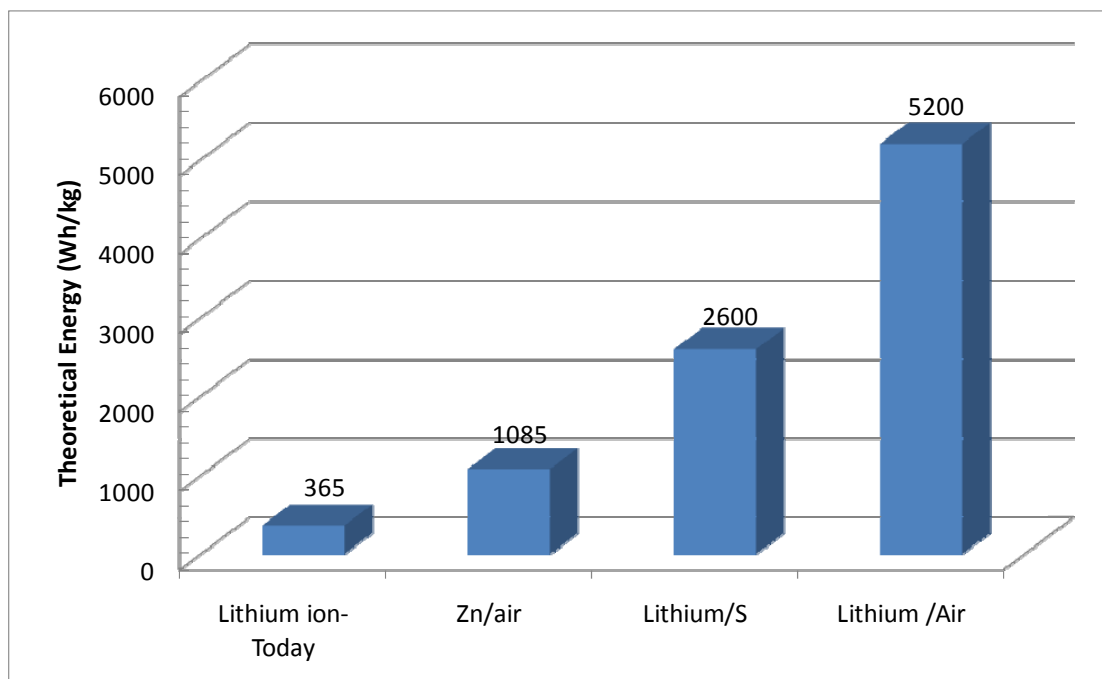


FIGURE 6. Theoretical specific energy (Wh/kg) of various electrochemical couples. All numbers are theoretical energy densities and accounts **only** for the weight of the active material.

CONCLUSIONS

Lithium-ion batteries offer many advantages that make them suitable for use in vehicular applications, including higher energy and power capability and, possibly, lower cost compared to Ni-MH cells. One significant advantage of the Li battery is that the chemistry (*i.e.*, materials for the anode, cathode, and electrolyte) are not fixed and a wide variety can be used, each of which can change the characteristics of the system. This provides battery researchers with additional degrees of freedom. However, with each choice, it has been observed that while some characteristics are improved, others prove lacking. No silver bullet has been found that can be considered an ideal Li chemistry.

While Li-ion is expected in HEVs in the very near future, use in PHEVs is expected to be more gradual and dependent on solving the life and cost challenges. Finally, batteries for pure EVs remain problematic because of the range and charging-time issue. A focus on higher energy systems would help decrease the \$/kWh. Similarly, the use of coatings and additives will play a large role in enhancing life. Safety remains a big concern with Li batteries, highlighted by the recent incidents plaguing the consumer electronics market. Both engineering and materials approaches are being pursued to address this challenge. Safety will remain in the forefront of any discussion of battery-powered vehicles and much care and attention is needed to ensure that no incidents occur that undermine this concept.

The future of batteries remains very strong and one can be optimistic as to the advances that will occur in this class of energy storage devices. Considerable improvements can still be made to the concept of a Li-ion battery, both in terms of finding new materials and in alleviating the limitations of existing systems. Batteries exist that promise tremendous improvements compared to the ones presently available; however there are significant challenges in commercializing these systems. The key to enabling these systems to operate with high energy, long life, and good safety characteristics lies at the interface. Modification of the interface will play an increasing important role in batteries in the near future.

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