Keeping up with the Increasing Demands for Electrochemical Energy Storage

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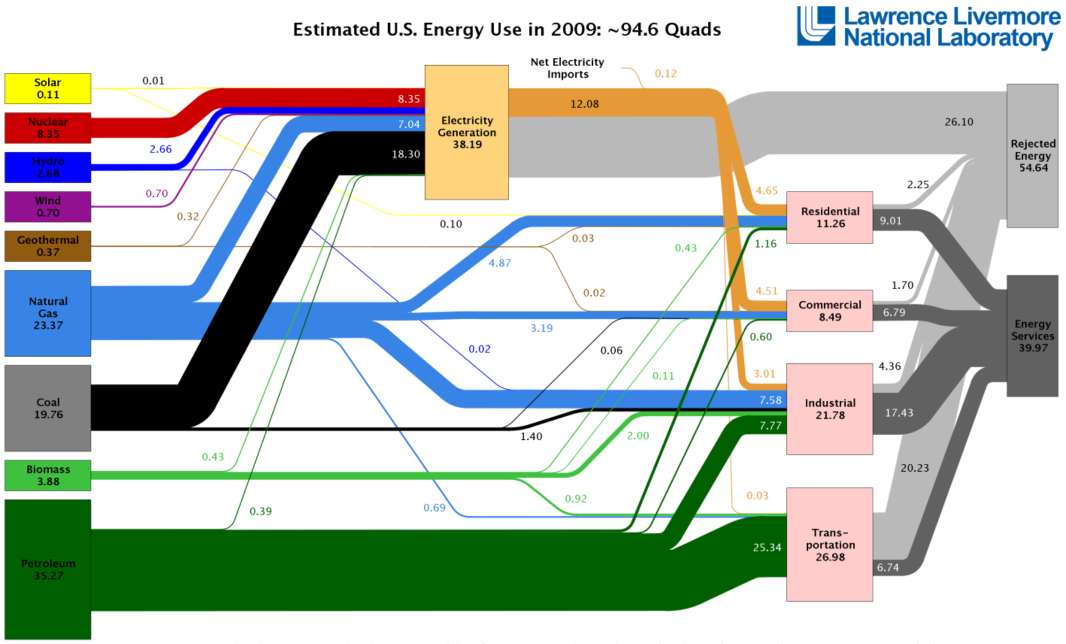
Abstract

The impetus for vehicle electrification is unprecedented. Several automotive manufacturers are currently producing or are planning to produce: hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV) and fully or battery electric vehicles (BEV). Currently, Li ion battery technology is the leading candidate to meet the near and midterm needs for electric vehicles. Leveraging considerable growth and development from the manufacturing of batteries for microelectronics, Li ion technology has advanced significantly in the last decade. However, the leap from small scale microelectronics batteries (tens of watt hours) to electric vehicle battery packs (tens of kilowatt hours) is not trivial. Performance metrics such as $/kilowatt hour, specific energy (Wh/kg), safety and cycle life are drastically more demanding for electric vehicles compared to laptop and cell phone batteries. While currently available electric vehicles (EV) show promise in minimizing the reliance on fossil fuels, widespread implementation of EVs will likely require a revolutionary advance in energy storage technology. This article provides an overview of energy storage technology for vehicle electrification, highlights the challenges and discusses future opportunities at the frontiers of battery research.

The need for advanced energy storage

From a sustainability perspective, minimizing the dependence on finite fossil fuel supplies and reducing CO_2 emissions are compelling arguments to electrify vehicles (EV).
From a practical perspective, electrifying vehicles makes sense based on an existing infrastructure for electrical power production and transport soon to be bolstered by our nation's efforts to augment renewable energy production where the primary byproduct is electrical power, i.e. photovoltaic cells and wind turbines for example. If electrical energy is the preferred form of energy, electrochemical energy storage is a natural fit. In contrast, hydrogen fuel cell technology requires an entirely new infrastructure to efficiently produce hydrogen, transport, store and re-convert it to electrical energy.

To put into perspective the amount of energy that is consumed by the transportation sector, out of the11.7 Terawatt-hours (1 Quad = 0.29 Terawatt-hours) of energy used by the US in 2009, 1.98Terawatt-hours (17%) of serviceable energy is consumed for transportation (Figure 1) [LLNL]. However, due to the relatively low chemical-to-mechanical energy conversion efficiency (33%) of internal combustion engine technology (ICE), 37% of the nation's rejected or wasted energy comes from transportation; a disproportionately large percentage compared to other sectors. Likewise, if EVs can improve energy efficiency in the short term and non-fossil fuel-based/renewable electrical power generation technology can be realized in the long term, the benefits to our country's current and future sustainability are clear. Assuming the latter, the following discussions will focus on electrical energy storage, specifically batteries.



Source: LLNL 2010. Data is based on DOE/EIA-0384(2009), August 2010. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for non-thermal resources (i.e., hydro, wind and solar) in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Figure 1: Energy use in the US in 2009 [https://energy.llnl.gov/informatics.php].

Challenges for electrochemical energy storage

Defining the ideal battery for EVs is complicated due to the numerous powertrain configurations that comprise HEVs, PHEVs and BEVs. For example, the capacity (kWh), power (kW), cycle life, etc… can be considerably different for an HEV compared to a BEV [Khaligh, 2010]. To simplify discussion, this article will primarily focus on BEVs with battery characteristics that can power a four-seat vehicle for approximately 100 miles on a single charge, in order to enable widespread adoption. Whether this BEV performance standard is what is required to significantly impact energy consumption is not precisely known at this time, however, agencies and auto companies are, in general, presently in agreement with this definition [CCC, Bruce, Thackeray 2012]. The vehicle range is determined by amount of energy stored in the battery and the rate at which the energy is extracted to propel the vehicle. A 23 kWh battery used to power a ~ 70kW electric motor is believed to be sufficient to achieve a ~160 km range. The mass and volume of the battery should be minimized to reduce the vehicle mass while maximizing vehicle cabin volume, respectively. Vehicle acceleration is determined by power density (kW) or how quickly the stored energy can be extracted. A common metric is in the single to multi kW/kg range. Replacing the ICE powertrain with an electric powertrain should not considerably add to the vehicle cost, likewise the battery pack cost should be < ~$5,000. Assuring the range of the vehicle is maintained throughout its lifetime requires a charging efficiency of 99.9999% such that ~80% of the original battery capacity is available at the end of the vehicle's life. Enabling widespread use requires operation in dramatically different climates in the US. Likewise, the battery must be capable of operating at relatively low and high ambient temperatures. Although it is difficult to quantify how fast is fast enough, the issue of range anxiety may be addressed if a battery pack can be charged at a charging station as fast as a gasoline tank can be filled at a gas station. Lastly, and perhaps most importantly, the battery technology must be safe and reliable.

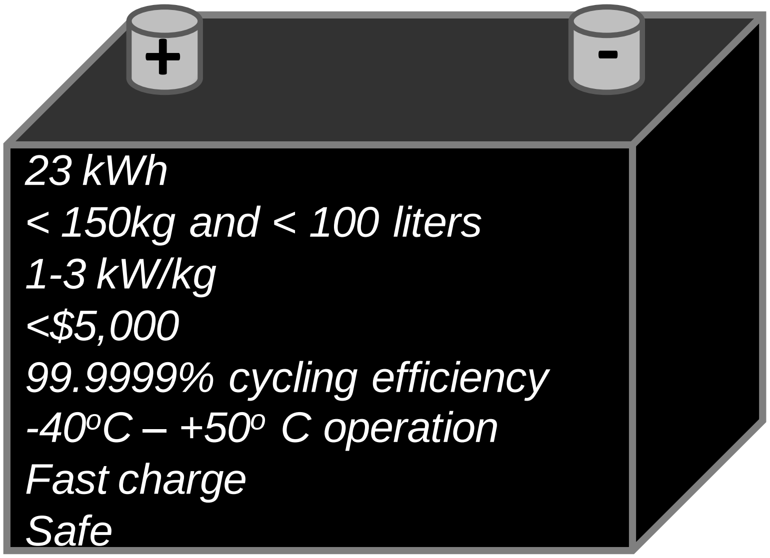


Figure 2: Battery performance criteria to power the next generation BEVs.

Li-ion batteries

Of the battery chemistries available today, Li-ion (Figure 3) has the highest specific energy [Tarascon, 2001] and is the only technology currently capable of meeting the criteria described in Figure 2. While other energy storage technologies such as supercapacitors, flywheels and compressed air are currently under development, no technology other than Li-ion batteries are mature enough or meet the necessary criteria or both [Dunn, 2011]. From a fundamental perspective, Li-ion batteries have the distinct advantage of intrinsically high cell voltage (>3V) combined with the ability to store ions in the solid-state rather than in the liquid state, resulting in high specific energy and low cell volume (energy density), respectively. In a typical Li-ion cell (Figure 4), Li ions are shuttled, with relatively high efficiency, between the anode and cathode via a liquid Li-ion electrolyte. Graphite (in powder form) is, by far, the most common anode that reversibly uptakes and releases Li-ions between graphene sheets. The cathode consists of a ceramic of nominal formula $LiMO_2$ (in powder form), where "M" stands for a transition metal like Co, Mn or Ni that can change valence states upon insertion/extraction of Li-ions. During discharge, it is more energetically favorable for the graphite anode to release its Li-ions and for the cathode uptake Li ions to reduce the transition metal "M" valence charge, e.g. M^{4+} to M^{3+}. This shuttling of Li-ions from the anode to cathode is accompanied by the simultaneous passing of an electron through an external circuit to do work.

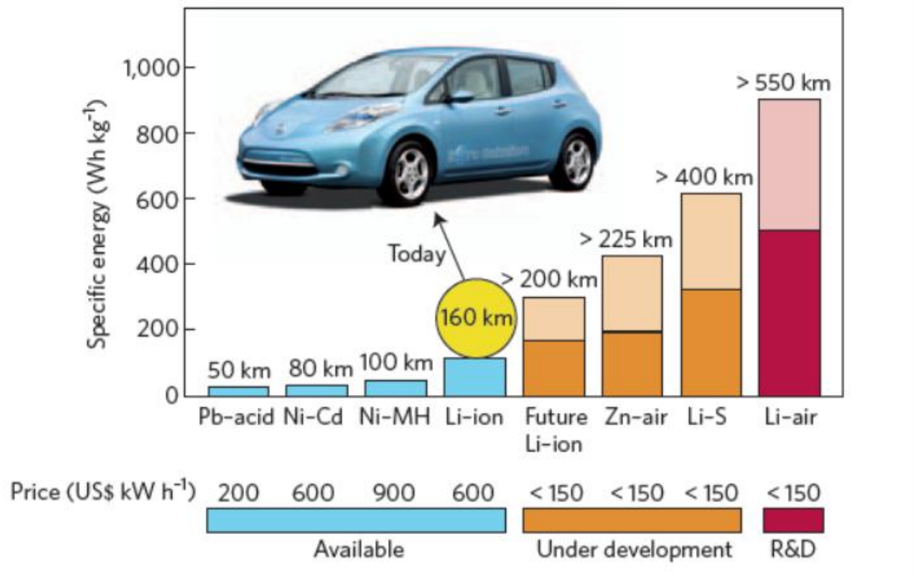
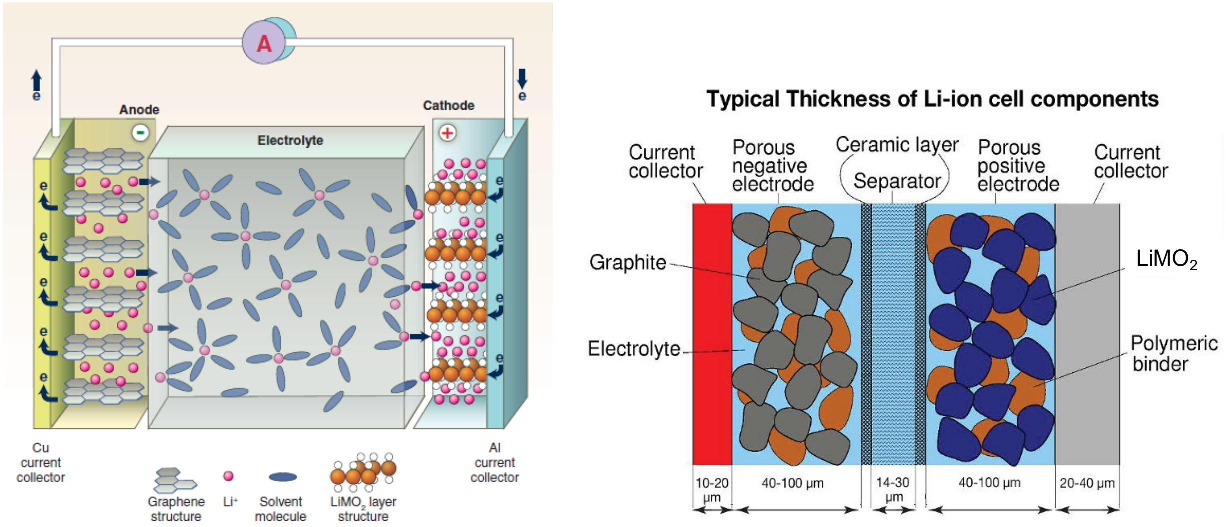


Figure 3: Comparison of battery technologies; currently available and under development [Bruce 2012].



(a) **(b)**

Figure 4: Schematic of a Li-ion cell: (a) at the atomic scale [Tarascon, 2001], (b) at the microscopic scale [SAE, 2012].

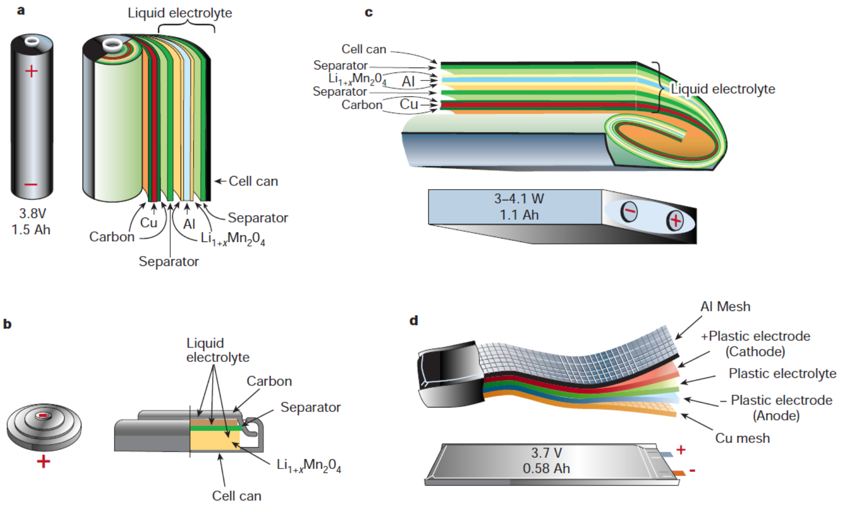


Figure 5: Li-ion batteries come in a variety of designs: (a) spiral wound cell, (b) button or watch cell, (c) prismatic cell and (d) solid polymer (electrolyte) battery [Tarascon, 2001].

Since the original invention by Sony and Professor John B. Goodenough in 1991, Li-ion batteries were quickly integrated into cell phones, laptop computers and other microelectronics (Figure 5). Incidentally, examples of some of the first Li-ion powered EVs were not terrestrial, but instead vehicles that were sent to survey the surface of Mars in 2003 (NASA Mars Exploration Program: [Huang, 2000]). The MER Li-ion batteries started development in 1996 and were flight qualified and placed on launch pads in 2003; a testament to how quickly Li-ion battery technology can progress. In 2008, a combination of factors led to significant push to improve vehicle fuel efficiency resulting in a rapid transformation of the auto industry with an emphasis on vehicle electrification. In 2011 GM rolled out the PHEV Volt, Nissan introduced the BEV Leaf and in 2012 Ford started selling the BEV Ford Focus. Indeed, these past and recent successes are impressive; however, Li-ion battery packs still require considrable reductions in cost and the specific energy must be increased to extend vehicle range. Addressing these issues, primarily from a materials perspective, is the focus below.

Opportunities at the frontiers of electrochemical energy storage

Unlike Pb-acid, Ni-Cd and Ni-MH battery technologies, Li-ion technology performance still has room for improvement as noted in Figure 3. Advanced electrode and cell designs and electrode material breakthroughs [Thackeray, 2012] may enable a doubling in energy density and four-fold reduction ion cost compared to the currently available Li-ion technology. Eventually, however, Li-ion technology improvements will crest requiring a breakthrough in battery technology to approach the cost target (~$150/kWh) and the range of an ICE powertrain vehicle (>400km). Several research and government agency reports [CCC, Bruce, 2012] are converging on a near term roadmap to guide battery research and development over the next two decades. Three milestones comprise the frontiers of battery development with substantial steps in 2015 and 2020 followed by a revolutionary leap in 2030. The details of each milestone are presented below with an emphasis on materials and materials processing.

2015 milestone: optimize current materials and cell component design

In the short term (by 2015) the focus will be on optimization of current materials and conventional liquid electrolytes. At present, approximately 50% [White, 1998] of a battery pack mass is dead weight. For example, in the cell cross-section shown in Figure 4b, only the graphite anode and $LiMO_2$ particles store Li and therefore energy. The current collecting foils, electrolyte, separator, hermetic container do not store energy. Therefore, increasing the mass/volume fraction of active material is one strategy to improve specific energy. Making thicker, less porous electrodes is one popular approach to achieve this. However, as active electrode layers get thicker and less porous, the transport of ions in the electrolyte is impeded, resulting in diminished ionic transport, i.e. reduced power [Novak, 2005]. Additionally, the non-uniform current in thicker electrodes can cause metallic Li to deposit on the anode and oxygen gas to be released from certain $LiMO_2$ cathodes, which can be a safety hazard in the presence of heat and flammable electrolyte solvents. Addressing these challenges could be achieved through research in advanced electrode designs, powder processing and coating technologies [DOE, 2012]. Cycle life is another issue that needs to be addressed. A passivation layer forms on the surface of a graphitic anode particle (solid electrolyte interphase: SEI). When Li intercalates/de-intercalates from graphite particles, swelling and contraction creates fissures in the SEI, resulting in the continuous and irreversible consumption of Li that leads to reduced capacity retention. Again, improved electrode designs to homogenize charge flow could address this issue as well as the development of new electrolytes and/or electrolyte additives to make the SEI more robust. Research in sophisticated and efficient power electronics, battery/cell telemetry, safety, thermal management and schemes to recycle/re-use EV batteries can help to establish a solid foundation for the electrification of EVs. From a cost perspective, it is believed that the economy-of-scale argument will not play a significant role in minimizing the $/kWh metric [CCC, Bruce, 2012] by 2015. It follows that new materials with appreciably higher performance and lower cost are needed to bring costs down to the ~ $150/kWh target.

2020 milestone: electrode and electrolyte materials breakthroughs

After the electrode and cell design have been optimized, increasing the specific energy requires new electrode and complementary electrolyte materials that can store more Li or charge-per-unit mass/volume and that have higher voltage (energy = Amps x Volts x time). If the new materials can be made at comparable or lower cost, a byproduct of increased specific energy is a commensurate decrease in $/kWh with the goal of $150/kWh (Figure 3). It is also important to note that the 2020 milestone seeks to realize the full potential of future Li-ion technology where the specific energy plateaus at approximately 300 Wh/kg enabling a 200 km range at a the targeted cost of $150/kWh.

Alloying anodes such as Si or Sn-based electrodes will likely comprise the next generation of Li-ion battery anodes [Thackeray, 2012]. The term “alloying” is used to describe the reversible, electrochemical reaction between Li and a pure element like Si or Sn. Specific capacity (mAh/g), which refers to the capacity or amount of Li that an electrode can uptake and release, is commonly used where one mole (6.94 grams) of Li can provide 26.8 Ah of electrical charge. Graphitic anodes have a theoretical specific capacity of 372 mAh/g. Si and Sn have specific capacities of 4009 and 960 mAh/g, respectively, making the interest in these anodes apparent However, a >300% change in volume accompanies the uptake and release of Li from Si and Sn, which creates significant mechanical stresses causing decrepitation and poor cycle life [Verbrugge, 2012]. One solution is to reduce the powder particle size from the typical micron scale to the nano scale, which decreases the magnitude of strain. Creating nano Si wires with < 100nm dimensions, originally demonstrated by Cui *et al.*, reduces the overall strain to minimize decrepitation and improving cycle life [Cui, 2012]. Another approach is to embed Si or Sn particles into an elastic or compliant carbon matrix to create an encapsulation effect thereby increasing cycle life [Kung, 2011]. Envia Systems recently claimed a 400 Wh/kg Li-ion cell pack using Si-based anodes, but it has yet to be commercialized [Thackeray, 2012]. Advanced materials processing and materials engineering could play a major role in optimizing alloying electrode performance and reducing cost.

On the cathode side, there are two promising approaches. First, the cathode system referred to as a composite layered structure, enables the full extraction of one mole of Li, or x = 1 per formula unit of $xLi_2MnO_3(1-x)LiMO_2$ (M = Mn, Ni, Co) [Thackeray, 2012]. This type of material, developed by Thackeray *et al.* at Argonne National Lab, can deliver nearly twice the specific capacity compared to conventional $LiMO_2$ cathodes. There are a few practical issues with this material strategy, however, to include the fact that the Li must come from the anode (unlike the case with conventional $LiMO_2$ cathodes) and the operation voltage (4.6 V) is outside the stability window of most conventional electrolytes, resulting in diminished cycle life. The second approach involves increasing the cathode reaction voltage from ~4.0V to ~5.0V to result in a 20% increase in specific energy, provided the specific capacity is comparable to conventional cathodes. Examples include $LiMn_{1.5}Ni_{0.5}O_2$ and $LiMPO_4$ (M = Co, Ni) [Allen, 2011]. These two examples are relatively mature compared to the composite layered cathodes described above, however, the lack of stable electrolytes prevent their implementation.

Increasing cell voltage (cathode side) and forming a stable SEI (anode side) with advanced anodes require large improvements in electrolytes. One approach is to integrate additives to conventional electrolytes to improve the high voltage (cathode) stability. There are some recent examples of success such as increasing the electrolyte stability to enable the use of $LiCoPO_4$ (4.8V) cathodes by Kang *et al*. [Kang, 2011]. A completely different approach involves a solid electrolyte material breakthrough where a ceramic electrolyte can be used rather than a liquid electrolyte. The advantages could include higher stability (0 to >6V) and perhaps safety in that a flammable liquid electrolyte is replaced by a highly thermal and chemical stable ceramic. A class of ceramics referred to as “fast-ion conductors” conduct Li ions about as fast as electrons move in a computer chip. Additionally, these ceramics have negligible electronic conductivity and the conductivity increases with increasing temperature. Recent examples of promising solid electrolytes include S (sulfur) based [Kamaya, 2011] and oxide-based electrolytes [Weppner, 2007, Sakamoto, 2011] that exhibit Li ion conductivities comparable to conventional liquid electrolytes.

The next generation Li-ion batteries will require new materials for anodes, cathodes and electrolytes. Advanced materials and ceramic processing technology, predictive capabilities combined with the lessons learned from the 2015 milestone will play a key role in achieving the 2020 milestone. The development of new electrolyte materials, in particular, will be a research area that will carry over into the 2030 milestone to enable new battery chemistry beyond Li-ion technology.

2030 milestone: beyond Li-ion batteries

A relatively new conference “Beyond Li-ion” started five years ago. Since its inception, attendance has grown significantly and for a good reason. If electric powertrains are to replace ICE technology, without changing the definition of transportation (no range anxiety), a new battery technology is required [Bruce, 2012]. Three of the most popular battery chemistries that represent the frontier of energy storage are: Li-S(sulfur), Zn-air and Li-air (the metal air batteries are actually semi-fuel cells, but for brevity and consistency with the community they will be referred to as batteries). Because the challenges related to Zn-air technology are relatively well known [Lee, 2011], this article will focus on Li-S and Li-air batteries which are not as well understood.

Li-S is attractive owing to its high theoretical energy density (2199 Wh/l), high theoretical specific energy (2567 Wh/kg) and the low cost and abundance of S [Bruce, 2012]. Factoring in the mass of the electrolyte, current collecting foils, packaging, etc., the practical specific energy is reduced to ~ 600 Wh/kg, which is still considerably higher than advanced Li-ion batteries. In a Li-S cell, elemental Li and S are the reactants, a non-aqueous electrolyte shuttles Li-ions between electrodes and, because S is not electrically conductive, specific carbon [Nazar, 2009] is added to increase the effective electrical conductivity of the S-cathode. Two of the major issues are: 1) preventing deleterious mechanisms that result from the formation of soluble LiS compounds during cycling and 2) achieving a stable/cycle-able Li-electrolyte interface. The latter issue led to the demise of rechargeable Li metal anode batteries in the 1980s and remains an issue.

Li-air batteries can be separated into two types [Bruce, 2012]. First, non-aqueous Li-air batteries involve the reaction of Li with oxygen gas (O_2) to form Li_2O_2. Hence, the common reference to "air" can be misleading since both water vapor and carbon dioxide must be excluded from the reaction/cell in the non-aqueous configuration. During discharge, Li is transported through a non-aqueous electrolyte and reacts with O_2 in the presence of a porous carbon network and a catalyst to form solid precipitates of Li_2O_2. The theoretical energy density of this system is (3436 Wh/l) and the theoretical specific energy is (3505 Wh/kg). Some of the key challenges for non-aqueous Li-air include: 1) development of an O_2 permeable membrane that excludes carbon dioxide and water vapor, 2) developing effective cathode electrodes that prevent pore occlusion resulting from the formation of solid byproducts during discharge AND effectively integrating catalysts to reduce overpotential upon charging. The second Li-air variant is aqueous-based. An aqueous electrolyte is used to transport Li-ions into a carbon cathode electrode to form LiOH during discharge. At lower concentrations LiOH is soluble in the electrolyte, but precipitates out as a solid at higher concentrations, i.e. greater degrees of discharge. The theoretical energy density of the aqueous variant is (2234 Wh/l) and the theoretical specific energy is (3582 Wh/kg). Some of the challenges that remain for aqueous Li-air technology are: 1) protecting the Li metal anode from the aqueous electrolyte using a ceramic electrolyte membrane, 2) preventing reactions with carbon dioxide from ambient air and 3) preventing pore and electrolyte interface occlusion when/if LiOH precipitates form at higher depths of discharge. Although there are few examples of advanced prototypes, the projected specific energy for both Li-air variants is expected to be in the 1000 Wh/kg range.
Indeed, the majority of the challenges involve the discovery of new materials and liquid electrolytes. Ceramic electrolytes are one aspect common to Li-air and Li-S technology. In addition to poor cycle stability, excess Li is required to counter the effects of poor cycling efficiency. For example, two to four-fold excess Li may be necessary to account for this issue, thus reducing the energy density. One recent material breakthrough in 2007 by Weppner *et al.* [Weppner 2007, Sakamoto, 2011] identified a new class of ceramic oxide electrolyte that is believed to exhibit the unprecedented combination of stability against Li with high, room temperature ionic conductivity. In addition to new electrolytes, advanced catalyst and catalyst support electrodes, similar to those found in fuel cells, are required to improve rechargeability and power.

Conclusions

There is a compelling need for advanced electrochemical energy storage to power the next generation of electric vehicles. Li-ion batteries offer substantial performance advantages over previous battery technologies; however, range anxiety and cost are major challenges to overcome in the short term (by 2015). Better electrode, cell and pack design along with advanced manufacturing and power electronics will establish a solid foundation for future EV technology. In the near term (by 2020) material and electrolyte breakthroughs are expected to provide moderate improvements in BEV range, but dramatic reductions in cost. Anodes that are cheap (based on Si, Sn and C) are expected to uptake and release more Li per unit mass. On the cathode side, the focus will be increasing the voltage and Li uptake and release per unit mass. Developing higher stability liquid and solid electrolytes will complement higher voltage cathodes and efforts to revolutionize energy storage in the long term (2030). Provided the necessary electrical infrastructure is in place by 2030, a breakthrough in electrochemical energy storage is required if ICE technology is to be replaced by BEVs. Metal-air or Li-S batteries may be the high specific energy, low cost technology of the future; however, significant materials and engineering challenges must be overcome. Solving the anode metal-electrolyte interface stability issue; developing novel catalyst/catalyst support cathodes; and stable, semi-permeable solid electrolytes will be the foci if metal-air and Li-S technologies are to mature. Clearly, the frontiers of electrochemical energy storage are exciting, from multiple perspectives, and are likely to generate significant engineering research and development opportunities in the coming decades.

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