Topic Paper #17

Advanced Batteries: "Beyond Li-ion"

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Advanced Batteries: “Beyond Li-ion”

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Introduction

Lithium-ion batteries are poised to enable the transformation of automotive drive from pure internal combustion engines to hybrid systems with limited but significant all electric range. The high energy and power density of today’s lithium-ion batteries are the result of nearly forty years of research and twenty years of commercial development. Despite these technical accomplishments, it is clear that long-term vehicle electrification – especially affordable 200 mile all-electric range – will require batteries with approximately three times greater energy densities at about one third the cost per kWh.

In this white paper, we survey electrical energy storage technologies that may be considered “beyond lithium ion” – these are the technologies which we believe have the potential to substantially alter the landscape of vehicle electrification. As an exhaustive review of the materials and systems research involved could potentially fill several volumes, we have chosen to focus on the potential impact, major challenges, and current research trends associated with these potential battery technologies. We have included references to more detailed, area-specific reviews where appropriate. We begin by reviewing research on materials for next-generation Li-ion batteries, which we expect will largely act as drop-in replacements for conventional materials. The expected performance of advanced Lithium-ion batteries set a realistic benchmark for the evaluation of the “beyond Li-ion” technologies. In our survey of beyond Li-ion technologies, we have evaluated both new chemistries and new device architectures. As many of these advanced energy storage technologies will require new manufacturing approaches, we do not attempt any quantitative cost estimates.

Several performance metrics used to describe energy storage systems include the specific energy [Wh/kg], specific power [W/kg], energy density [Wh/L], and power density [W/L]. When citing one of these descriptors, it is important to be clear on what mass and volume has been included in the calculation. A significant fraction of the mass and volume of a battery suitable for integration into a vehicle is occupied by ancillary equipment that monitors and manages the temperature and health of the battery. Thus, in engineering specifications, the mass and volume must reflect the full packaged system; for electric vehicle applications we refer to this as the **pack level**. For research and development purposes, it is convenient to define these metrics using only the mass and volume of a particular set of active materials; we refer to this as the **materials level**. At all levels of integration, the rate capabilities of energy storage systems are compared after normalizing for total capacity: the rate is specified as *C/n* where *n* is the number of hours for full (dis)charge (*e.g.* a C/2 charge takes 2 hours to accumulate the full theoretical capacity). A final, commonly reported materials-level metric is the specific capacity (the amount of charge stored per unit mass of active material) given in engineering units of mAh/g. While not directly translatable to pack-level metrics, the materials-level metrics help guide laboratory scale research in identifying promising materials that can eventually be integrated into battery systems.

The United States Advanced Battery Consortium (USABC) has developed several pack-level technical targets for the long-term development of commercially viable electric vehicles. Several of the key long-term PHEV-40 and BEV pack-level targets are listed in Table 1; these goals were developed to enable electrified vehicles that are cost-competitive with internal combustion engine vehicles and do not reflect that status of existing battery technologies. Clearly, the BEV goals are much more technically demanding – and demand much lower cost – than the PHEV-40 metrics [1]. Hidden in these targets is an important tradeoff between pack energy and cycle life: to achieve the same number of end-of-life electric miles, the higher capacity BEV battery needs to survive fewer deep discharge cycles than the smaller capacity PHEV battery. For example, a BEV with a 200 mile all-electric range will reach 100,000 electric miles after 500 cycles while a PHEV-40 battery must endure 2500 cycles to reach the same 100,000 electric-powered miles.

Table 1: USABC Long-term pack-level technical targets

Vehicle class	**Pack Energy (kWh)**	**Cycle Life (# cycles)**	**Specific Energy at C/3 (Wh/kg)**	**Energy Density at C/3 (Wh/L)**	**Cost ($/kWh)**
PHEV-40 (High Energy/Power)	11.6 (at 10kW)	5000	97	145	300
BEV	40	1000	200	300	100 (<150 as "minimum for long-term commercialization")

As these engineering targets are framed at the pack-level and most research is performed at the materials level, it is important to appreciate how materials-level improvements translate to the pack-level. Vehicle packs based on conventional wound or stacked Li-ion batteries rely on three separate packaging steps (materials to cells, cells to modules, and modules to packs) between material and packs. *This is currently necessary but fundamentally undesirable because each packaging step dilutes the pack-level energy density and specific energy.* First, the active materials are mixed with binder and conductive carbon additives, cast onto metallic current collectors to make composite electrodes, which are then stacked or wound along with a separator and filled with liquid electrolyte, and finally sealed hermetically into **cells**. Since a complete pack may have hundreds of cells, a secondary level of packaging is typically employed whereby a smaller number of discrete cells are bundled into **modules**. Note that Li-ion batteries are unique in requiring a discrete cell, unlike lead-acid batteries, which are directly assembled at the module level. Finally, modules are gathered in a **pack** that can be used in a vehicle. The module and pack provide protective housing with power electronics for temperature control, state of health monitoring and regulation.

As a concrete example of the materials-to-pack specific energy dilution, we consider a commercial 2.9 Ah 18650 cell (a cylindrical cell 18mm diameter and 65mm long) as an indicator of today's state of the art Li-ion cell. We assume the working electrochemical couple is $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 \parallel C_6$ (a so-called "NMC – graphite" cell), which has theoretical materials-level specific energy of 557 Wh/kg and energy density of 1800 Wh/L [2]. At the cell level, the manufacturer's specifications report practical values of 236 Wh/kg (42% efficient) and 620 Wh/L (34% efficient) [3]. At the module and pack levels, the specific energy and energy density are again substantially diluted. The pack-level specific energy of the Nissan Leaf and Tesla Roadster are both ~120 Wh/kg [4]; the Chevy Volt pack has an energy density of ~100 Wh/L (based on the 10.4 kWh usable energy). The cell-to-module-to-pack integration is anticipated to become more efficient as pack designs are refined and prismatic cells displace cylindrical cells for automotive applications, but the pack-level energy density and specific energy will continue to be substantially diluted relative to the materials-level.

The most aggressive obstacle to the development of commercially viable long-range (>200 mile) battery electric vehicles is the cost per kilowatt-hour of storage [$/kWh]. While we do not attempt to quantify costs in this white paper, we can identify two main **materials-level** specifications which should be improved to drive down per-kWh costs; specifically, materials-level research should identify materials with 1) intrinsically high energy density and specific energy and 2) low cost and high abundance [5]. At the systems level (cell, module, and pack), new, more mass and volume efficient device architectures are required to fully harness the energy density of the available active materials.

Materials for Next Generation Lithium-ion Batteries

We begin by reviewing the anode and cathode active materials that have a high likelihood of being implemented in the next generation of lithium-ion batteries. The materials reviewed in this section are expected to act as drop-in replacements in conventional Li-ion device architectures and thus we can use the materials-level characteristics to roughly project cell and pack-level performance metrics. We first survey positive electrode ("cathode" materials) and then negative electrode ("anode") materials.

Advanced Cathode Materials

To achieve higher energy Li-ion batteries, cathode materials with higher specific capacity, higher voltages, or both must be identified and successfully developed. Three main classes of potential drop-in replacement, high-energy Li-ion cathode materials have emerged – oxygen release materials, 2-electron systems, and high voltage cathodes.

Oxygen Release Cathode Materials

"Oxygen release" materials are a class of lithium storage positive electrode materials displaying high specific capacities of 220-280 mAh/g during electrochemical cycling between 2-4.8V. These materials offer a theoretical materials-level energy density of > 4000 Wh/L and a specific energy > 900 Wh/kg (throughout this article, theoretical values are taken to be with respect to a Li^0 electrode). *With successful development as a drop-in replacement for conventional positive electrode materials, these materials can meet the PHEV-40 targets and may play a role in enabling all-electric BEVs.* We use the term "oxygen release" to encompass all materials that share a common feature of reversible capacity gain upon oxygen evolution during the first charge cycle. These compounds are also variously referred to as 'composite' cathode materials, 'layered-layered' composite, 'layered-spinel' composite, and 'lithium excess' cathode materials. These materials have compositions with a general formula $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiMO_2}$ ('layered-layered') or $x\mathrm{Li_2MnO_3}\bullet(1-x)\mathrm{LiM_2O_4}$ ('layered-spinel') where M = Cr, Mn, Co, or Ni. In each case, initial charging to a voltage > 4.5 V [vs. Li^+/Li] removes lithium to the negative electrode with oxygen ions being removed from the initially inactive Li_2MnO_3 component, "activating" it for subsequent electrochemical cycling with added storage capacity [6]. The initial oxygen removal does not appear to have any deleterious effect on the negative electrode of full cells [7].

Chronologically, the published record shows early work at Dalhousie University having demonstrated the high capacity of these materials.[8-11] Extensive subsequent work at Argonne National Laboratory further developed and extended the general approach[12-16]. At least five companies including LG Chem, BASF, General Motors, Toda Kogyo and Envia Systems have announced licensing agreements with ANL related to these cathodes. Today, these materials are the subject of intense research and development internationally, at universities, national laboratories, and companies [17].

While these materials offer a factor of 1.5-2 increase in materials-level energy density compared to phosphate and other oxide cathodes, several challenges remain, including 1) first cycle irreversible capacity loss (up to ~40 mAh/g), 2) limited performance at high rates (low power density) [18-20], 3) capacity fade after moderate cycling [21] and 4) 'voltage fade' – a declining average discharge voltage over extended cycling.

Of these problems, the voltage fade issue may be the largest remaining barrier. Voltage fade in these materials occurs as the Mn-rich layered material formed during the 'activation' apparently undergoes a structural transformation to a spinel-like structure during extended cycling [21,22]. This transition can be suppressed by increasing the fraction of transition metal cations known to stabilize the layered structure, such as Co and Ni, but this increases materials cost. Voltage fade causes reduced energy efficiency and complicates battery management due to the evolving voltage of the cell. Similar irreversible structural transformations are known to occur in other Mn-rich layered materials synthesized by conventional methods [23-27]. Recent evidence suggests that voltage fade can be reduced by alternative synthetic routes that help to stabilize the layered structure [28] or by surface coatings [20].

'Two-Lithium' Cathode Materials

Another trend in lithium-ion cathode research is the search for compounds that can reversibly (de)intercalate two lithium ions per transition metal, offering the promise of nearly doubled specific capacity compared to existing cathode materials. These materials must have a transition metal capable of a +2 change in formal valence upon charge and discharge. Challenges for these systems are stability, kinetics, and minimizing the voltage separation between the two distinct redox processes so that the cell voltage over which capacity is accessible is not too wide. Three main classes of materials with the potential for two lithium cycling have been identified: 1) silicates, 2) tavorite-structured materials, and 3) pyrophosphates. It is notable that no stably cycling 'two-lithium storage' compound has yet been demonstrated.

Lithium storage silicates of the general formula Li_2MSiO_4 (M = Fe, Mn, Co) have theoretical capacities in excess of 200 mAh/g [29] and adopt a large number of polymorphs. Early reports on iron silicate Li_2FeSiO_4 appeared in 2005 [30] and reversible capacities of 120-140 mAh/g were later demonstrated [29,31]. Elevated temperatures were required for high rate testing, indicating slow kinetics in these materials. Despite promising theoretical capacities and voltages, the manganese [31,32] and cobalt [33] silicates have also been challenged by rapid capacity fade.

A wide variety of potential two-lithium compounds are isostructural to the natural mineral *tavorite* $LiFe(PO_4)(OH)$[34]. Lithium tavorites encompass a broad range of chemical compositions with the general formula $LiM(TO_4)X$ where M is a redox active metal, *T* is a p-block element, and *X* is O, OH, or F [35]. A high-throughput computational evaluation of tavorite-structured oxyphosphates, fluorophosphates, oxysulfates, and fluorosulfates for use as cathode materials in lithium-ion batteries identified four compounds, $V(PO_4)F$, $MoO(PO_4)$, $WO(PO_4)$, and $NbO(PO_4)$, as the most promising two-electron candidates [35]. Among all the screened compounds, $Li_2Mn(PO_4)F$ has the greatest overall theoretical energy density [3708 Wh/L] and specific energy [1218 Wh/kg]. Experimentally, two lithium cycling has not yet been demonstrated in tavorite materials; the demonstrated capacity of $LiFeSO_4F$ at a C/10 rate is only 130 mAh/g [36]. The use of these materials as sodium-ion storage compounds will be discussed in a later section.

A third class of potential two-lithium cathode materials is the pyrophosphates $Li_2MP_2O_7$ (M = Fe, Mn, Co) [37-40], for which a recent review surveys the materials which have been explored to date and gives some potential directions for future study [41]. Even if two-lithium cycling cannot be demonstrated, these materials may be interesting as high voltage cathode materials [42]. For the Fe and Mn pyrophosphates, theoretical calculations predict that the second lithium can only be extracted at voltages > 5V, for which practical electrolytes do not yet exist [39]. As with tavorites, experiments to date have demonstrated capacities corresponding to only one lithium atom per transition metal.

High-Voltage Spinels

High voltage spinels increase specific energy primarily by raising cell voltage rather than capacity. Manganese-rich spinels based on $LiMn_2O_4$ have been commercialized that operate near 4V with capacities of ~110-130 mAh/g. The operating potential can be raised by replacing Mn with an alternative transition metal that serves as the main redox center, leaving the Mn ions as inert stabilizers [43]. Of particular interest is the nickel manganese spinel $LiMn_{1.5}Ni_{0.5}O_4$, which operates at 4.7 V on the Ni^{2+}/Ni^{4+} couple with a theoretical capacity of 147 mAh/g. The moderate capacity combined with low crystallographic density does limit the increase in volumetric energy density that is possible. Nonetheless, if current technical issues can be solved, this compound has potential as a drop-in cathode in low-cost, high specific power HEV and PHEV systems.

This material faces two primary challenges. Firstly, it must be synthesized under precisely controlled thermochemical conditions to obtain the desired crystal structure and electrochemical cycling characteristics. Secondly, the high voltage strategy inherently requires that the electrolyte possess electrochemical stability in practical cells at up to 5 V vs. Li^0. With current electrolytes, the usable cycle life is inevitably limited by electrolyte oxidation at such high potentials.

Depending on synthesis conditions, the nickel manganese spinel $LiNi_{0.5}Mn_{1.5}O_4$ exhibits varying degrees of order among the Ni and Mn ions. The highly ordered and highly disordered materials have markedly different transport properties and electrochemical performance, with the disordered material being generally preferred [44-46]. Several research groups have attempted to stabilize the disordered phase by additional cation doping. For example, allowing titanium to substitute for manganese stabilizes the disordered phase, slightly increases the operating voltage, and – for low titanium concentrations – improves the cathode's rate capability by increasing the diffusivity of lithium [47]. Capacity retention can be increased by substituting chromium, iron, cobalt or zinc on a combination of Mn and Ni sites; such doping also decreases the lattice mismatch between two coexisting phases that appear with delithiation, thereby improving the mechanical stability of the material [48].

Strategies employed to stabilize the cathode in contact with normally unstable electrolytes include surface-segregating dopants and surface coatings. Aliovalent dopants such as zinc and iron can segregate to the cathode particle surface[49], where they may suppress electrolyte oxidation reactions and prevent the formation of high-impedance surface layers. Similarly, electrolyte oxidation reactions can also be suppressed by surface coatings with materials such as zinc oxide [50], aluminum tri-fluoride [51], and bismuth oxide [52].

Advanced Anode Materials

The graphite anode enabled the development of today's lithium-ion batteries by replacing lithium metal, which has safety and life issues associated with lithium dendrite formation during cycling. At the same time, it did not sacrifice much operating voltage. While the specific capacity of graphite, 372 mAh/g, is higher than the cathodes with which it is paired, graphite also has a relatively low crystallographic density of 2.25 g/cm^3 that limits capacity density to 837 mAh/cm^3. Alternative anodes based on silicon and tin (see Table 2) provide theoretical specific capacities and capacity densities that are up to a factor of 10 higher. Even at currently attainable capacities that are well short of the theoretical limits, no other drop-in active material under consideration has as high an impact on the cell-level energy density. The primary hurdle in developing practical high capacity anodes has been the large volume expansion upon lithiation, which limits cyclability, due to the loss of electrical connection to particles and the consumption of working lithium in the solid-electrolyte interphase (SEI). Conventional alkyl-carbonate based electrolytes are thermodynamically unstable against reduction below about 1V vs Li/Li$^+$, causing the formation of SEI. Whereas in graphite anodes this passivation layer can be thin and stable, in alloy anodes the massive volume change upon cycling leads to fracture that further exposes unpassivated alloy, resulting in continued consumption of working lithium and electrolyte solvent. Various strategies for stabilizing alloy anodes have been explored in the past decade, and it seems that silicon anodes with reversible specific capacities in the range of 600-1000 mAh/g appear close to commercial implementation.

Table 2: Comparison of Graphite, Tin and Silicon Anodes

Material	**Limiting Composition**	**Average Voltage vs. Li†/Li (V)**	**Theoretical Specific Capacity (mAh/g)**	**Theoretical Capacity Density (Ah/L)**	**Volume Strain at Theoretical Capacity (%)**
Graphite	LiC_6 [53]	0.1 [53]	372	760	12.8 [53]
Tin	$Li_{4.4}Sn$ [54]	~0.4 [55]	992	7,240	260 [56]
Silicon	$Li_{4.4}Si$ [57]	~0.3 [55]	4,200	9,660	310 [56]

Several distinct approaches have been used to improve the cycling stability of alloy anodes. First, it has been shown that electrochemical lithiation of silicon causes the formation of metastable amorphous Li-Si alloy rather than the equilibrium crystalline intermetallic phases [58]. Cycling within a limited capacity and potential range that preserves the amorphous phase extends cycle life [59], hence the avoidance of crystallization has developed as one design strategy. Second, the use of nanostructured forms including nanowires[60], self-assembled composites [61,62], and nanotubes[63] has been used to improve specific capacity and cycling stability. Up to 6000 cycles at capacities ~1000 mAh/g have been demonstrated [64]. The use of nanostructures raises questions, not yet resolved, regarding the volume packing density achievable in practical electrodes, the reactivity of ultrahigh surface area materials under abuse scenarios, manufacturing scalability, and cost. A third general approach is to support the 'active' alloy anode material with an 'inactive' stabilizing material [65-6762] This improves cycle life but naturally dilutes the capacity of the electrode. The silicon-based anodes that are nearing commercialization are primarily based on silicon or silicon alloy particles interspersed in, or deposited on, a graphite support. Cells using interspersed tin/cobalt alloy anodes were briefly available in consumer electronics from about 2006 [68]. Cells prepared with these anodes have a high volumetric energy density of about 478Wh/L when cycled slowly at C/6, but significant capacity fade and limited rate capability[69]. Further, the relatively high cobalt content of these materials made them too costly for automotive applications[70]. One strategy to decrease the cost of these microcomposite anodes is to replace some of the cobalt by iron[71].

A likely trajectory of development for silicon-based anodes is initial insertion in the marketplace at a fraction of the theoretical capacity (e.g., 600-1000 mAh/g) and with cycle life adequate for consumer electronics (~500 cycles). A marginal improvement in energy density (~20%) over graphite-based lithium ion may be sufficient to justify commercialization. Over time, specific capacity will systematically improve although the inherent volume change does not allow theoretical capacity density to be reached at the electrode level. Table 3 illustrates the increase in cell-level energy density that would result assuming use of current NMC cathodes with Si anode at specific capacities ranging from 500 to 2000 mAh/g. (The cell model assumes capacity-matched cathode and anode, allows electrode thickness to vary up to a maximum thickness of 100 μm, and includes the mass and volume of the current collectors, porous composite electrodes, separator and electrolyte.) Successful implementation of silicon anode at 1000 mAh/g and 2000 mAh/g respectively increases the cell-level energy density by 27% and 37%. These are "nameplate" values and the usable energy in automotive applications may be as low as one half of these numbers depending on restrictions in depth of discharge that may be made to achieve power and life metrics. Assuming that usable pack energies are 50% of the cell value, comparison with Table 1 shows that PHEV-40 requirements of 97 Wh/kg and 145 Wh/L are easily met (Table 1), the BEV specific energy target of 200 Wh/kg is not quite within reach, and the BEV energy density target of 300 Wh/L should be attainable.

Table 3: Cell-level specific energy and energy density upon replacing graphite (baseline) with silicon anode at various specific capacities, assuming an NMC cathode

System	**Anode Specific capacity (mAh/g)**	**Specific Energy (Wh/kg)**	**Energy Density (Wh/L)**
NMC || Graphite (baseline)	372	236	620
NMC || Si	500	250	668
NMC || Si	750	267	728
NMC || Si	1000	277	763
NMC || Si	1500	289	801
NMC || Si	2000	292	821

Summary of Impact of Drop-in Replacement Electrodes on Next Generation Li-ion:

Taking into account the above-discussed improvements in next-generation cathodes and anodes, projected values of the materials-level and cell-level specific energies and energy densities are illustrated in Tables 4 and 5, respectively. In each case a Si anode having 1000 mAh/g reversible capacity is assumed. As above, the cell-level values are "nameplate" rather than "usable" energies. As one point of validation, the projected cell-level specific energy of ~400 Wh/kg for oxygen release cathode coupled with 1000 mAh/g silicon anode is in good agreement with recently announced results for demonstration cells using this couple developed under ARPA-E support [72]. Discounting by a factor of two from cell to pack level allows this chemistry to just meet the 200 Wh/kg BEV target (Table 1). Although in theory Li_2MnPO_4F and $Li_2MnP_2O_7$ could also meet the target, experiments are less encouraging that facile two-lithium reactions can be achieved in practice. Thus, there are very limited options for meeting the long-term USABC BEV pack level targets using currently known drop-in replacement electrodes in the existing Li-ion pack architecture. A significant improvement in the cell-to-pack integration efficiency from the current value of ~50% would allow additional developing chemistries to meet the BEV targets. The PHEV targets are less challenging, and are well within reach for next-generation lithium ion.

Table 4: Materials-level specific energy and energy density for advanced cathodes paired with Si anode (at 1000 mAh/g specific capacity). NMC-graphite is given as a baseline for comparison (first row).

System	**Specific Energy (Wh/kg)**	**Energy Density (Wh/L)**
$LiNi_{1/3}Mn_{1/3}Co_{1/3}$ || Graphite (baseline)	557	1800
$0.3Li_2MnO_3 \bullet 0.7LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$	744	2850
$LiNi_{0.5}Mn_{1.5}O_4$	591	2344
Li_2MnPO_4F *	933	2654
$Li_2MnP_2O_7$ *	702	1990

* Assuming reversible capacity of 2 Li per transition metal

Table 5: Cell-level specific energy and energy density for advanced cathodes paired with Si anode (at 1000 mAh/g capacity). Values for commercial NMC-graphite cells and from our cell model are given for comparison (first row).

Cathode material	**Specific Energy (Wh/kg)**	**Energy Density (Wh/L)**
$LiNi_{1/3}Mn_{1/3}Co_{1/3}$ || Graphite (baseline)	231 (calculated) 236 (commercial product)	599 (calculated) 620 (commercial product)
$0.3Li_2MnO_3 \bullet 0.7LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$	403	1256
$LiNi_{0.5}Mn_{1.5}O_4$	316	1011
Li_2MnPO_4F *	435	1169
$Li_2MnP_2O_7$ *	400	1089

* Assuming reversible capacity of 2 Li per transition metal

Electrochemical Energy Storage Beyond the Li-ion Paradigm

We now turn to electrochemical storage technologies that while less proven, could bring about a paradigm change for electric transportation. Below, approaches are considered that fundamentally differ from the Li-ion approach of using storage compounds that intercalate or alloy with lithium. "Beyond Li-ion" does not necessarily imply a Li-free chemistry, however, since the low operating potential, low specific mass, and low specific volume of lithium continue to make it an extremely attractive working ion. We provide brief reviews of each of the following: 1) elemental metal anodes, 2) metal – air systems, 3) the lithium – sulfur battery, 4) displacement reaction Li cathodes, 5) non-Li rocking chair systems, 6) organic lithium storage materials, and 7) flow systems.

Elemental Metallic Negative Electrodes

Among possible battery negative electrode materials, the elemental form of the working ion provides the highest capacity and cell voltage. Such electrodes can be used against positive electrodes of various kinds ranging from conventional lithium-ion intercalation cathodes to the air cathode in metal-air batteries and the sulfur cathode in metal-sulfur couples. The specific capacity (mAh/g) and capacity density (mAh/cm^3) of Li, Na, Mg, Zn, and Al elemental metallic electrodes are summarized in Table 6.

Table 6: Comparison of Elemental Metallic Anodes

Element	**Valence**	**Molar mass (g/mol)**	**Density (g/cm^3)**	**Specific Capacity (mAh/g)**	**Capacity Density (mAh/cm^3)**
Li	1	6.941	0.53	4634	2456
Na	1	22.99	0.97	1166	1131
Mg	2	24.31	1.74	2205	3837
Zn	2	65.41	7.14	820	5851
Al	3	26.98	2.70	2980	8046

The challenge of developing a practical, stably cycling elemental anode varies widely among these materials. For example, durable metallic lithium anodes remain an elusive target due to the formation of dendrites (high surface area "mossy lithium") that can be the origin of safety events and also result in poor cycling efficiency associated with SEI formation on the exposed lithium[70,73]. In contrast, recent interest in magnesium ion chemistry is largely driven by the observation that Mg metal can be cycled with good reversibility and morphological stability in certain electrolytes[74,75].

Strategies adopted to enable the use of elemental metal negative electrodes include the use of inorganic, organic, or composite solid electrolytes, alternative liquid electrolytes or electrolyte additives, or alloying of the elemental electrodes to promote stable cycling.

Many different inorganic solid electrolyte compositions have been investigated since the 1970s[76-78]. Interest today focuses on lithium lanthanum titanate perovskites (LLTO)[79], LISICONS (NASICON-related phases) such as $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP)[80,81] and $Li_{2+2x}Zn_{1-x}GeO_4$[82], thio-LISICONS such as $Li_{4-x}Si_{1-x}P_xS_4$[83,84], oxide garnets[85,86], and glassy lithium phosphorous oxynitrides (LiPON)[87-89]. Broad challenges for inorganic solid electrolytes include limited room-temperature conductivities and inadequate chemical stability at either the anode or cathode. For example, some Ti^{4+} in LATP is reduced to Ti^{3+} upon contact with Li metal, increasing the material's electronic conductivity. Improvements in room temperature ionic conductivity may be possible, as the recently discovered $Li_{10}GeP_2S_{12}$ solid electrolyte material has room temperature ionic conductivity of ~12 mS/cm – greater than conventional liquid electrolytes[90].

Organic solid electrolytes generally fall into two classes, (dry) polymer electrolytes and gel (or hybrid) polymer electrolytes[91]. In dry polymer electrolytes[92,93], a salt is dissolved in high molecular weight polymer such as polyethylene oxide (PEO) or polyvinylidene fluoride (PVDF). In gel (or hybrid) polymer electrolytes[94], liquid electrolytes such as the typical alkyl carbonates are added to lower the melting temperature and increase the volume fraction of amorphous polymer. To inhibit lithium dendrite growth, solid electrolytes must have a high mechanical stiffness (about twice the modulus of Li metal)[95]; for inorganic phases this is trivially satisfied, but for organic solid electrolytes, mechanical stiffness is inversely correlated with ionic conductivity. The block copolymer electrolytes[96] being developed by SEEO promise to decouple ionic conductivity from the mechanical stiffness potentially enabling higher conductivity, mechanically robust polymer electrolytes.

Hybrid solid electrolytes that use both polymeric and organic electrolytes in multilayer or dispersed configurations have also been suggested. Most notably, PolyPlus is developing a suite of multilayer electrolytes using LISICON solid Li-ion conductors to enable the use of Li-metal negative electrodes[97].

An alternative approach to stabilizing lithium metal electrodes is the development of new liquid electrolytes (solvents and salts) or electrolyte additives that promote more uniform high-density Li-metal deposition[98]. There is evidence that chlorosilanes react with lithium metal to form a protective surface layer[99]; direct silane coatings on lithium metal anodes have been shown to stabilize cycling out to ~100 cycles[100]. Other suggested paths to stable lithium metal anodes include the use of room temperature ionic liquid electrolytes, which do not form SEI at the Li/Li^+ potential – though the cost and ionic conductivity of ionic liquid electrolytes remain a concern[101] – or the use of Na/Li[102] or Mg/Li[103] alloy electrodes

For metallic negative electrodes to substantially improve cell-level energy densities compared to intercalation or alloy anodes, it is imperative that the excess metal be minimized. For example, if 300% excess Li is required for successful deployment, electrochemical couples utilizing Li metal anodes have lower energy density than a 1000 mAh/g silicon anode. On the other hand, elemental metallic negative electrodes are an enabling technology for the metal-air batteries discussed in the next section.

Metal-Air Batteries

Batteries built to harness metallic oxidation reactions, using atmospheric oxygen as a cathode, have been a prized goal of energy storage research for decades. Including the mass of the oxygen reactant, metal-air batteries have exceptionally high materials-level theoretical specific energies (Table 7), which in the case of Li-air exceeds that of current lithium-ion battery couples (e.g., NMC/graphite, Table 4) by nearly a factor of ten. However, there are numerous challenges that must be overcome to enable reversible cycling of metal-air cells with high energy efficiency, as well as challenges in system design to take advantage of the intrinsically high energy. Currently, the system-level specific energy and energy density are difficult to assess, due to lack of detail as to the mass/volume of complete cells and balance of plant that would together constitute a practical system.

Several metal/air couples have been evaluated for use in rechargeable batteries, as indicated in Table 7. While Zn-air batteries have been used since the 1970's as cheap, high-energy primary (non-rechargeable) cells, no secondary (rechargeable) metal-air system has yet been commercialized. The bulk of research has been aimed at the lithium-air system due to its exceptionally high theoretical specific energy. A comparison with the practical energy density of gasoline in modern cars is useful. The tank-to-wheels efficiency of gas-powered cars is today about 17%, resulting in a practical gasoline energy density of 2244 Wh/kg (theoretical energy density of 13,200 Wh/kg). The battery-to-wheels efficiency for current lithium-ion powered EVs is about 50%, and would likely be lower for rechargeable metal-air due to lower roundtrip efficiency. Assuming 40% battery-to-wheels efficiency in an optimized metal-air system, the system-level energy density required for parity with gasoline is 5610 Wh/kg. This exceeds the theoretical specific energy of all but Li-air; and in all cases, system level values will be significantly discounted from the values in Table 7. Nonetheless, the possibility of exceeding the long-term BEV targets (Table 1) as well as the energy density of advanced lithium ion (Table 5) by a factor of several at system level has driven much recent research in metal-air.

Table 7: Metal-Air Systems

Metal	**Theoretical Specific Energy (Wh/kg)** *Including Oxygen Weight*	**Demonstrated**
Lithium	5,200	Limited Reversibility
Aluminum	4,300	Primary Cell
Zinc	1,090	Limited Reversibility
Silicon	3,960	Primary Cell
Gasoline (Reference)	13,200 (2244 practical)	-

Metal/Air cell Data from reference [104]

Silicon data based on specific energy given in [105]*, recalculated to include oxygen weight*

Metal-air batteries typically have a cell architecture that consists of a pure metal anode, a solid or liquid electrolyte, and a conductive nanostructured cathode in contact with gaseous oxygen. The challenges associated with the use of elemental metallic anodes have been summarized in a previous section. In addition, there are challenges for the cathode and electrolyte that must be overcome to enable efficient cell operation. A critical component of all metal-air batteries is the air cathode. Typically, it consists of a nanoporous carbon network immersed in a liquid electrolyte with interpenetrating gas phase. The liquid electrolyte can be aqueous or non-aqueous, and this choice has a large influence on the reaction pathways and products. On discharge, metal ions diffuse through the electrolyte and electrons are conducted through the carbon scaffold while oxygen gas diffuses or is pumped into the porous structure. This design produces a large number of triple phase boundaries where electrolyte, oxygen gas, and conductive carbon meet so that metal ions, electrons and oxygen are all locally supplied. For non-aqueous cell chemistries, metal oxide is precipitated onto the carbon scaffold as the reaction proceeds; in aqueous cells, the reaction product is often soluble in the electrolyte.

We now summarize progress and challenges for specific metal/air systems.

Lithium-Air

Since the first report on rechargeable lithium-air batteries in 1996[106], the high theoretical energy density and specific energy of the Li/O_2 system has captured the interest of many researchers. While substantial progress has been made toward the development of secondary Li/O_2 cells, many challenges remain[107-114]. Most research to date has focused on non-aqueous Li/O_2, where the Li metal electrode is generally assumed to be protected from atmospheric water and carbon dioxide by the liquid electrolyte. Aqueous Li-air is also feasible if the Li metal can be isolated from the aqueous electrolyte by a solid electrolyte.

In the case of non-aqueous Li/O_2, a stable electrolyte must first be identified. The discharge products are highly sensitive to electrolyte composition[115-119], and carbonate electrolytes in particular show high, irreversible, chemical reactivity with the lithium peroxide (Li_2O_2) discharge product, preventing reversible cycling [120-124]. A second, but closely related problem is the high voltage hysteresis between charge and discharge. The extremely high charging potentials are due in part to the undesired decomposition products, as evidenced by the observation of CO_2 evolved during recharge [122]. Ether electrolytes are more stable than carbonates, but not sufficiently stable for commercial development [117,125]. Furthermore, there is evidence that the carbon scaffold used in the air cathode also reacts chemically with the discharge products.

The second major problem facing non-aqueous Li/O_2 is the quality of the oxygen supply. Non-aqueous Li/O_2 electrochemistry is particularly sensitive to contamination by CO_2 and H_2O. While it is reasonable and appropriate to perform research on Li/O_2 electrochemistry using highly purified O_2 from tanks, such a tank dramatically decreases the practical energy density and specific energy of practical Li-air batteries. Preliminary systems estimates for a Li/O_2 battery requiring an O_2 tank suggest the Li/O_2 system has lower energy density than advanced Li-ion batteries (though the Li/O_2 system retains a greater specific energy)[110]. For “open” systems (i.e. without an O_2 tank), the inlet air stream must be highly purified with an on-board filtration system. A lithium –sulfur /oxygen hybrid battery has been proposed to reduce the poisoning sensitivity of air cathodes.[126]

Even if these practical issues are resolved, the inherent kinetics of Li_2O_2 formation and reduction reactions may be sluggish as evidenced by limited power capability. Lithium-air cells often discharge at about 2.6 V but charge at 4 V or higher, with round trip energy efficiency below 70%. Atomistic models of Li_2O_2 deposition suggest that about 1 V of this hysteresis is caused by the activation energies of the Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER)[127,128] which might be mitigated by using an appropriate catalyst. Several possible catalysts have been suggested, including manganese oxides[129,130] of varying structure and composition, iron, copper and cobalt oxides[131], and platinum and gold[132-134]. While these catalysts have improved the energy efficiency of these cells to >70%, there is a large gap to reach the >90% round-trip efficiency of lithium-ion cells. The electronic conductivity of the Li_2O_2 peroxide also seems to be low, though the exact conduction mechanism is not been resolved [135,136].

Sodium-Air

Room temperature Na/O_2 cells appear to exhibit many of the same problems as the better studied Li/O_2 cells, such as dendrite formation and electrolyte reactivity. However, as the melting point of sodium is relatively low at 98°C, these cells have the potential to be run with a molten Na electrode at temperatures which are relatively low compared to other molten electrode cells. Such cells have recently been demonstrated[137]. A recent review[138] offers perspective on this and other Na cell designs.

Aluminum-Air

Aluminum-air batteries have been demonstrated as primary cells, but little research has been performed to make them reversible. The tendency of Aluminum to form a thin Al_2O_3 diffusive barrier on its surface prevents efficient plating. There is less of an incentive to make Al-air batteries reversible due to the low cost of metallic aluminum. A life-cycle analysis suggests that using a ‘mechanically rechargeable’ Al-air battery system could prove cost-effective[139].

Hydrogen production due to anode corrosion by the electrolyte is the most pressing problem in these cells. It can be mitigated somewhat by introducing some alloying elements into the aluminum anode[140], or by using electrolyte additives which cause it to slow[141]. Impurities such as iron can speed the corrosion process however, and could increase the cell cost by requiring high-purity anodes.

Zinc-Air

Zinc-air batteries have been used since the 1970’s as cheap, high energy density primary cells. Work has begun in the past several years on identifying catalysts and cell architectures for increased capacity and potential reversibility, and on preventing anode degradation[142].

Silicon-Air

The silicon-air cell has been proposed as a cost effective battery with a specific energy comparable to that of Al-air[105]. Silicon is corroded rapidly by aqueous solutions, but non-aqueous electrolytes could allow a pure silicon cathode to reach a stability that would make these cells possible. A primary silicon-air cell has recently been reported, and further development appears promising[143].

Rechargeable metal/air batteries with high energy density are today far from commercialization. A key challenge for researchers is to identify and focus efforts on metal/air systems that will offer substantial energy density improvements at the systems level. The systems-level challenges – and potential for energy density dilution – may vary enormously among different metal-air chemistries. For example, while the Li/O_2 couple is extremely sensitive to CO_2 and H_2O poisoning, it is not yet known ifthe Al/O_2 or Si/O_2 systems are equally sensitive. Therefore, it is reasonable to expect that the gas handling requirements for different metal-air systems may be extremely different. The basic electrochemistry needs further elucidation before systems-level energy densities can be estimated for the metal-air systems other than Li/O_2.

Lithium-Sulfur

Lithium-sulfur batteries are based on the electrochemical reaction $16Li + S_8 \leftrightarrow 8Li_2S$ which has a theoretical specific energy of 2500 Wh/kg and a theoretical energy density of 2800 Wh/L. *If successfully developed, Li/S battery systems can meet both the PHEV-40 and BEV targets.* Sulfur is attractive as a cathode material because it is light, abundant, and environmentally benign. Three main obstacles have limited attempts to harness this tremendous potential [144,145]: 1) the poor electronic conductivity of elemental sulfur and the reaction product Li_2S, 2) the high solubility of polysulfide compounds Li_2S_x ($1 \leq x \leq 8$) that form as reaction intermediates, and 3) the large volume change ~78% upon full lithiation of sulfur. To successfully develop Li/S batteries, these challenges must be solved *while maintaining high sulfur loading* in the cathode (>50% by mass). Recent advances in Li/S research have been summarized in several recent review articles [109,146].

Electronic conductivity limitations have been overcome at the laboratory scale by intimate nanoscale mixing of sulfur with conductive carbon [147]. Such strategies allow high utilization of the sulfur cathode > 1300 mAh/g [148] and allow moderate rate cycling [149-151]. However, the practicality of such an approach in to large-scale cells is unclear; mesoporous carbon comprises nearly half the volume of the composite electrodes in some of these designs, drastically limiting the achievable energy density at the cell level. Recently, several groups have explored the possibility of using conductive polypyrrole polymer coatings [152,153] to promote more stable electronic contact in composite sulfur cathodes. However, to date, there has been no public demonstration of a lithium/sulfur cell with both excellent rate capability and excellent capacity retention – the ‘known’ solutions for these challenges appear to be contraindicated at present.

The ‘polysulfide problem’ is particularly onerous - these soluble species chemically attack the lithium metal negative electrode causing rapid capacity fade [144,145,154-156] Proposed solutions for eliminating the problems caused by polysulfides include identifiying electrolytes with limited solubility[157-160], use of solid electrolytes, and incorporation of additives that suppress polysulfide mobility [160,161]. Solid electrolytes, such as those developed by PolyPlus and Sion Power have been proposed to shield the lithium metal negative electrode from polysulfide attack, though this strategy does not directly address potential capacity fade due loss of active material at the positive electrode. To avoid the use of metallic lithium at the anode, several groups have proposed the use of high capacity alloy anodes, with pre-lithiation of either the anode or the cathode. Such Li-ion type cells with sulfur as a cathode material have been demonstrated using both solid polymer[162,163] and liquid [164] electrolytes.

Displacement Reaction Cathodes

Conventional lithium storage compounds operate by intercalation of lithium ions into a largely inert host structure. Displacement, or conversion, electrodes, on the other hand, undergo reconstructive phase transformations when reacting lithium. Upon lithiation a displacement reaction cathode undergoes a chemical substitution, which leaves a two-phase product consisting of a lithium compound and a pure transition metal. Transition metal compounds of this type have potentially high specific capacities and energy densities [165,166]. However, many such materials are poor electronic conductors, limiting rate capability, and the reconstructive phase transformations make efficient long-term cycling difficult.

Displacement reactions span many chemistries, including oxides, fluorides, phosphides, nitrides and sulfates. Research has concentrated on fluorides and oxides, which exhibit capacities far higher than those of conventional cathode materials [166]. Table 8 lists several possible conversion reaction materials that have been studied for lithium storage along with their theoretical materials-level specific capacity and capacity density.

Table 8: Selected conversion reactions for lithium storage

Material	**Reaction**	**Theoretical Specific Capacity (mAh/g)**	**Theoretical Capacity Density (mAh/cm^3)**
Cobalt (II, III) Oxide	$Co_3O_4 + 8e^- + 8Li^+ \rightarrow 3Co + 4Li_2O$	890	5440
Iron (III) Fluoride	$FeF_3 + 3e^- + 3Li^+ \rightarrow Fe + 3LiF$	712	2508
Carbon Fluoride	$CF + e^- + Li^+ \rightarrow C + LiF$	864	-
Copper (II) Fluoride	$CuF_2 + 2e^- + 2Li^+ \rightarrow Cu + 2LiF$	528	2233
Titanium (III) Fluoride	$TiF_3 + 3e^- + 3Li^+ \rightarrow Ti + 3LiF$	767	2607
Copper (II) Oxide	$CoO + 2Li^+ + 2e^- \rightarrow Co + 2Li_2O$	715	4613

The major challenges for displacement cathodes are reversibility of the reconstructive phase transformations and limiting voltage hysteresis between charge and discharge. Reversibility of the two-phase lithiation reaction is difficult first because the resulting heterogeneity can cause extensive fracture and second because metal diffusion is required to reverse phase separation. Thus, reversing the reaction entails an extra step which may prove rate-limiting depending on the electrode morphology. If phase separation occurs over long length scales it may be impossible to resorb all the metal, leading to an incomplete delithiation reaction and capacity fade.To promote facile reversibility, various nano-morphologies have been explored, including composite nanoscale matrices[167] and "nanoflower" catalysts used to functionalize nanowires[168]. High-performance nanowire arrays have been demonstrated with a capacity of 600 mAh/g at a high (20C) rate[169].

The second major challenge for displacement cathode materials is limited rate capability. At modest discharge rates (~1C), the cell voltage hysteresis can easily reach 1 V. Such inefficiency is a result of both the low inherent electronic conductivity of displacement reaction materials, and the considerable overpotential required to reverse the displacement reaction. These two problems will likely need to be solved simultaneously with the metal extrusion issue, by developing an electrode morphology which incorporates conductive pathways and catalysts to alleviate polarization while preventing large-scale phase separation. All of these strategies are in an academic research stage, with no announced commercial developments to date.

Alternative Working-Ions

As an electrochemical working-ion, lithium is attractive because it is light and highly mobile in solid hosts. In the long-term, cost, abundance, and volumetric energy density considerations may favor alternative working ions. Sodium chemistries are of interest due to the very high natural abundance of sodium; magnesium, zinc, and aluminum chemistries offer very high theoretical energy density (Wh/L) due to the polyvalent working ions (Mg^{2+}, Zn^{2+}, Al^{3+}) and potential use of elemental metallic negative electrodes; each also has greater natural abundance than lithium. Here, we survey potential alternative working ions for rechargeable batteries.

Sodium

The enormous natural abundance of sodium suggests the potential for low-cost sodium-based batteries. In the 1970s, sodium intercalation materials were investigated alongside lithium-storage materials, but were ultimately abandoned in favor of lithium systems. Despite the chemical similarity between sodium and lithium, to enable sodium ion systems, new cathodes, anodes, and electrolytes must be identified and optimized. Several recent reviews have surveyed work to date on sodium storage materials [138,170-172] and electrolyte challenges [173].

Due to the molar mass difference between lithium and sodium, it would be reasonable to expect that sodium systems will always have lower specific energy than a lithium analog. In practice, however, some sodium layered sodium transition metal oxides can be cycled reversibly over a wider composition range[174,175] than their lithium analogs, thus enabling higher specific capacities approaching 200 mAh/g. Nonetheless, when traded off against the lower average working voltage – 0.18–0.57 V lower for Na than for Li in the same host structure[176] – the specific energies are nearly identical.

Identification of high energy density anodes for sodium-ion batteries may be more challenging than it has been for lithium. Na analogs of the high capacity alloy anodes identified for Li-ion batteries may not be viable given that the molar volume increase upon sodiation is nearly twice as large as that for lithiation. Experience with lithium alloy anodes suggests that composite electrodes can tolerate a total electrode volume change limited to 100%; applying the same criterion would limit the obtainable energy density of sodium anode alloys to half that of the Li analogs [177]. Alternative choices include hard (*i.e.* disordered) carbon anodes, which have specific capacities up to ~300 mAh/g [178], and $Na_2Ti_3O_7$ which has a capacity of 200 mAh/g and an average potential of 0.3 V vs. Na^+/Na^0. New electrolyte solutions will be required for the commercialization of carbonaceous Na-intercalation anodes, as the passivation layers formed by $NaPF_6$ appears to have poor thermal stability[179].

Magnesium

Magnesium is an attractive alternative to lithium as a working ion with plentiful abundance and high theoretical energy density (Wh/L). The major challenge for magnesium batteries is to identify high energy density cathode materials that are compatible with electrolyte solutions that have been demonstrated to enable stable cycling of Mg metal anodes Alternatively, it may be possible to use oxide cathode materials with the alkyl carbonate electrolytes conventionally used in Li-ion batteries if an appropriate non-metallic anode can be identified.

Prototype magnesium batteries that survived thousands of electrochemical cycles were demonstrated in 2000[75], an accomplishment that is fundamentally due to the ability of magnesium electrodes to undergo reversible electrochemical stripping and plating. This is in stark contrast to lithium systems[180], where the development of a stable, reversible, elemental metallic electrode has not yet been achieved despite decades of effort. As discussed earlier, the use of elemental negative electrodes benefits both specific capacity and cell voltage.

While magnesium electrolytes with wide electrochemical windows (> 3V) have been developed[181,182], suitable high-energy-density magnesium cathode materials that operate with these electrolytes have remained elusive[183]. The most studied positive electrode material to date is Chevrel-phase Mo_6S_8 which has been demonstrated at a practical capacity of 122 mAh/g and high density (5.21 g/cm^3), but operates at a low average voltage of 1.1V vs. Mg/Mg^{2+} and has limited rate capability. Alternative materials such as MoS_2[184], $MgFeSiO_4$[185] and $MgMnSiO_4$[186] have been researched, but these materials still have relatively low theoretical energy density due to either limited capacity (< 200 mAh/g) or low average voltages (~2 V vs. Mg^{2+}/Mg). Sulfur has also been suggested as a possible high energy-density cathode material for magnesium batteries, though there is not currently a suitable electrolyte that is stable with both Mg metal and sulfur.[187]

Aluminum

The aluminum-ion battery has been proposed to capture the high potential specific energy of the trivalent ion. A preliminary Al-ion battery has been demonstrated using a metallic aluminum negative electrode and a spinel $Al_xMn_2O_4$ positive electrode with a theoretical specific energy of 1060 Wh/kg[188].

Zinc

A zinc-ion battery has been introduced in 2011, based on an α -MnO_2 insertion cathode and Zn alloy anode[189]. The first generation cathode material obtains a low-rate specific capacity of 210 mAh/g and maintains ~140 mAh/g during extended cycling at a 6C rate. The discovery of reversible Zn metal electrodeposition in a mild acidic electrolyte is also notable.

To compare the potential specific energy and energy density of these alternative working-ions, we estimate the theoretical energy density of hypothetical transition metal oxide (MO_2) intercalation cathodes paired with elemental metallic negative electrodes. The resulting estimates for cathode specific capacity and theoretical specific energies and energy densities are summarized in Table 9. As a point of comparison, we have included an identical estimate for Li in the first row of Table 9. These hypothetical cathode specific capacities represent aggressive estimates compared to existing demonstrations, but are not theoretical limits. For purposes of estimating the cathode specific capacity, we assumed that the average transition metal atomic mass is equal to that of titanium. We assume that Na, Mg, and Zn can be intercalated to one ion per transition metal and Al can be intercalated to 2 ions per 3 transition metals. For all chemistries, we assumed a cathode crystallographic density of 5 g/cm^3 and cell voltages of 4V, which assumes that appropriate advanced electrolytes with wide electrochemical stability windows can be developed. As a point of validation, there is good agreement (< 30% error) for the estimates of Li-ion specific energy and energy density with the theoretical values for high-energy Li-ion cathode materials.

Based on this analysis, we believe that sodium-ion batteries can approach but not exceed the energy density of lithium-ion batteries. The polyvalent systems (Mg, Zn, and Al) all have potential specific energy and energy density exceeding those of lithium-ion systems.

Table 9: Estimated theoretical energy density for hypothetical alternative working ion batteries, assuming an intercalation cathode and a metallic negative electrode. A hypothetical Li system is included in the first row for comparison.

Working ion	**Hypothetical Cathode Composition**	**Hypothetical Cathode Specific Capacity (mAh/g)**	**Estimated Specific Energy (Wh/kg)**	**Estimated Energy Density (Wh/L)**
Li (baseline)	$LiMO_2$	310	1240	6180
Na	$NaMO_2$	260	1040	5210
Mg	$MgMO_2$	515	2060	10290
Zn	$ZnMO_2$	370	1480	7380
Al	$Al_{2/3}MO_2$	500	2010	10030

Organic Storage Electrodes

Research on lithium and sodium organic electrodes has been motivated by the possibility for "green chemistry" with low environmental impact [190], including the use of commodity materials currently produced in large quantities [191]. During the past several years, a substantial amount of research has been focused on developing organic insertion compounds that can be paired to make fully organic rechargeable cells. No consensus has been reached as to which chemical or class of chemicals holds the most promise. Numerous organic polymers and small molecules have been tested; the basic electrochemical properties of several materials are summarized in Table 10. Much of the challenge lies in finding a stable electronically conductive polymer or molecule with simultaneously a high redox potential and capacity. Many polymers and small molecules are able to intercalate lithium at intermediate voltages of 2V - 3.5V. For a high energy cell, a voltage of 4V is preferable. However, the formaldehyde and acetylene based compounds able to intercalate lithium at this voltage tend to have lower capacities.

Table 10: Organic Intercalation Compounds

Chemical Class	Voltage vs. Li^+/Li (V)*	Capacity (mAh/g)†	Demonstrated Cyclability, Rate
Cathode Polymers			
Imides [192]	2.5	175	100 Cycles at C/5
Formaldehydes [193]	4.2	100	30 Cycles
Acetylenes [194]	3.7	100	100 Cycles, 20% capacity fade
Dimercaptothiadiazoles [192]	2.8	375	Solubility-limited
Benzoquinone [192]	3.0	340	Low conductivity requires conductive additive
Cathode Small Molecules			
DMBQ [195]	2.6	275	10 cycles, 10% capacity fade
Chloroanilate [196]	2.3	125	25 cycles, still unstable
Anodes			
Terepthalate [197]	0.9	250	50 Cycles, 20% capacity fade
Dicarboxylate [198]	0.7	170	50 Cycles, 15% capacity fade

*Voltages given are approximate averages over charge/discharge cycles and are highly dependent upon the precise molecule used. See the papers cited for more detailed information.

† Capacities given are estimates based on the papers cited, and depend on the precise molecule used.

For transportation applications, the largest obstacle faced by this entire class of materials is their low density, which translates to low energy density at both materials and device levels. Other issues include the tendency of organic molecules to be unstable in the presence of oxygen, which suggests that manufacturing in inert atmosphere may be required, and high solubility in electrolyte solvents. Some otherwise promising active materials – such as poly(dimercaptothiadiazole) – upon dissolution undergo deleterious side reactions. Approaches aside from the development of compatible solvents include anchoring the active material to a substrate [199]. Clearly, even if the use of transition metals in the storage electrode is eliminated, lithium remains a relatively high cost component. This has motivated work on sodium organic electrodes [200-202]. However, the energy density limitations make this general approach probably better suited for stationary storage applications than for transportation.

Flow Systems

Redox flow batteries are rechargeable systems in which solutions of redox-active ions or complexes constituting a “catholyte” and “anolyte” are stored within separate external reservoirs and pumped into an ion-exchange/electron-extraction power stack[203]. Aqueous-chemistry flow batteries are of interest for stationary applications due to their scalability, safety, and relatively low cost ($250-$450/kWh depending on the specific chemistry). The flow battery architecture is unique in allowing the decoupling of power components from energy-storage components, thereby providing greater flexibility in the tuning of power vs energy than is available in stationary battery designs. However, aqueous flow batteries have inherently low energy density since the electrochemical couple is limited by electrolysis to ~1.5V cell voltage, and by low solubility of the redox species (typically 1-2M), the product of which yields ~40 Wh L^{-1} energy density for the fluids alone.[203] With low energy density fluids, hardware costs escalate, and the large fluid volumes that must be pumped produce parasitic mechanical losses that detract significantly from round-trip efficiency.

Transportation applications for flow batteries become realistic only if the energy density of the flowable electrodes is increased by an order of magnitude or more. One new approach capable of meeting this target, recently developed at MIT [204], is called a semi-solid flow cell (SSFC). Instead of attempting to increase the solubility of *solution* electrodes, this approach embraces insolubility in the form of *suspension* electrodes. For example, solid storage electrodes such as those used in lithium ion batteries have storage energy densities which in molarity units range from 21M (e.g., graphite) to 51M ($LiCoO_2$) to 189M (silicon), so that even at suspension concentrations allowing flowability (e.g., 50 vol%), the energy density is more than tenfold greater than typical aqueous redox solutions. Combined with the 2-3 times higher cell voltage of nonaqueous electrochemistry, the MIT work projects system-level energy densities of 300-500 Wh L^{-1} and specific energy 130-250 Wh kg^{-1}. Other developments in high energy density flow batteries include zinc flow air battery (ZFAB) described by ReVolt Technology that uses a flowable zinc electrode to prevent the growth of zinc dendrites, as well as improvements in the air electrodes and catalysts dispersed in the electrolyte.

Conclusions

For the next 5-10 years, improvements in energy storage technology for electrified vehicles will be primarily driven by the roll-out of advanced Li-ion technologies utilizing new cathode and anode materials that are in the R&D pipeline today. For PHEVs, long-term specific energy and energy density targets should be easily met with drop-in replacement cathodes or anodes, and current industry roadmaps project that the cost target ($300/kWh) will be met as well. BEV performance and cost targets are much more challenging. The BEV specific energy and energy density targets cannot be achieved by improvements in cathodes or anodes alone, but *may* be met with simultaneous improvements in both. On the anode side, the most promising developments are in high-capacity silicon-based negatives. Industry R&D in silicon-based anodes is widespread, and the release of commercial products for portable electronics seems imminent, although simultaneous achievement of high capacity and sufficient cycle and calendar life for automotive applications remains to be demonstrated. Assuming the replacement of graphite anodes with silicon-based anode at 1000 mAh/g specific capacity, cell-level specific energy of 280 Wh/kg (an improvement of 17% over state-of-the-art Li-ion) and energy density of 760 Wh/L (a 19% improvement) are possible with no change at the positive electrode.

Among numerous drop-in cathode technologies, the oxygen release cathode materials have a large potential impact on energy density and are closer to commercialization than alternatives. The commercial viability of this class of cathodes hinges on progress in solving the voltage fade problem along with improvements in irreversible capacity loss and rate capability. Assuming success, the combined use of silicon-based anode and oxygen release cathode projects to cell-level specific energy of ~400 Wh/kg and energy density of ~1260 Wh/L. Other drop-in replacement cathodes such as the high voltage spinels based on $LiNi_{1/2}Mn_{3/2}O_4$, are more likely to impact PHEV or HEV technology where the emphasis is on power more so than energy. Two-lithium materials such as silicates, tavorites and pyrophosphates are theoretically attractive for BEV, but still face steep materials-development curves.

Poor cell-to-pack design efficiency further handicaps today's technology. To enable truly affordable long-range electric mobility, materials-level energy density improvements must be married with improved integration strategies that drastically reduce the mass, volume, and cost of ancillary components.

Moving beyond the USABC targets for BEV commercialization will require a deeper shift in battery chemistry and/or architecture to "beyond Li-ion" technologies. Quantitative projections of pack-level performance characteristics are currently difficult for these earlier-stage technologies. However, there are several alternatives which have the *materials-level potential* to be true game changers. A current assessment of the leading contenders is as follows. First, the Li-sulfur system may with sufficient development meet the BEV specific energy targets, but are unlikely to meet the energy density targets due to the inherently low density components and the high carbon loadings currently required to obtain good rate capability. Displacement electrodes have a chance of meeting gravimetric and volumetric BEV requirements, but their thermodynamic irreversibility will likely lead to a low round-trip efficiency. Among alternative working ions, sodium may eventually allow lower cost systems with specific energy and energy density comparable to today's Li-ion; the polyvalent systems of magnesium, zinc, and aluminum have high theoretical energy if the metallic negative electrodes can be used. Metal/air systems and high-energy-density flow batteries require fundamentally new system architectures with substantial engineering challenges, but offer significant potential for improvement over Li-ion at the pack-level. For metal/air batteries, the air handling and delivery components are expected to substantially lower the system-level energy density and specific energy from their very high materials-level values; given the current nascent stage of technology development, system level energies cannot be projected with confidence. Finally, organic electrodes may have cost and manufacturing advantages but are unlikely to meet transportation energy density requirements.

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