

Electrical energy storage for transportation—approaching the limits of, and going beyond, lithium-ion batteries

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The escalating and unpredictable cost of oil, the concentration of major oil resources in the hands of a few politically sensitive nations, and the long-term impact of CO₂ emissions on global climate constitute a major challenge for the 21st century. They also constitute a major incentive to harness alternative sources of energy and means of vehicle propulsion. Today's lithium-ion batteries, although suitable for small-scale devices, do not yet have sufficient energy or life for use in vehicles that would match the performance of internal combustion vehicles. Energy densities 2 and 5 times greater are required to meet the performance goals of a future generation of plug-in hybrid-electric vehicles (PHEVs) with a 40–80 mile all-electric range, and all-electric vehicles (EVs) with a 300–400 mile range, respectively. Major advances have been made in lithium-battery technology over the past two decades by the discovery of new materials and designs through intuitive approaches, experimental and predictive reasoning, and meticulous control of surface structures and chemical reactions. Further improvements in energy density of factors of two to three may yet be achievable for current day lithium-ion systems; factors of five or more may be possible for lithium–oxygen systems, ultimately leading to our ability to confine extremely high potential energy in a small volume without compromising safety, but only if daunting technological barriers can be overcome.

1. Introduction

Today, in developed nations, the supply and availability of energy are taken for granted. The simple turn of a switch produces light or heat, electronic communication is instantaneous, and an assumed supply of gasoline enables mass transport on a global scale. The burgeoning growth of the world's population and the expectation from underdeveloped countries for an equal stake in the earth's resources and quality of life are unsustainable without dramatic

improvements in the control and efficiency of energy production, storage, and use. Life's comforts over the past two centuries have been derived largely from the discovery and exploitation of fossil fuels, and the result of profound scientific and technological innovations. Whereas the creation of oil, coal, and natural gas reserves—the primary fuels for transportation—occurred over several hundred millions of years, we are on course to consume these non-renewable energy sources within several hundreds of years. Notwithstanding the unknown medium-to-long term implications of burning carbonaceous fuels and CO₂ emissions on a warming planet, it is abundantly clear that scientific and technological solutions are urgently required to avert a looming energy crisis of epic proportions.

The primary candidates as alternatives to fossil fuel are hydro-electric, nuclear, and renewable. Hydro-electric power is a clean source of energy, but it requires storing the potential energy of

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Broader context

State-of-the-art lithium-ion batteries, with a specific energy of ~150 Wh kg⁻¹, do not yet have sufficient energy or life for use in electrified vehicles that would match the performance of internal combustion vehicles. This review article summarizes, in a historical context, the characteristics and performance of lithium-ion batteries that are on the market for transportation applications, as well as more advanced lithium batteries that are in various stages of development. The implementation of a practical lithium–oxygen cell, which offers prospects of providing five or more times the energy density of today's lithium-ion systems, is being thwarted by daunting technological challenges.

water in dams in localized regions of the world and the transmission of power over restricted distances. Nuclear energy has its own set of challenges: in particular, long-term storage of waste that will remain radioactive for thousands of years and management of safety, especially in the wake of the Fukushima disaster. Renewable sources offer potential game-changing clean energy, but they are intermittent, whether they come from the sun, wind, or waves. These systems all would benefit from powerful energy storage units, like high-energy batteries, to properly balance source variability with the substantial variability in demand for power.

Electrical energy storage in the form of batteries can be used not only as a back-up energy supply for the national electric grid and smart grids for localized communities, but also as the power source



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for transportation, defense, or aerospace applications, as well as for smaller devices such as consumer electronics (e.g., laptops and cell phones), medical implants (e.g., pacemakers, defibrillators, and pumps), power tools, and toys. Batteries are now a commodity of national and strategic significance in a highly competitive international arena.^{1,2} Electrical energy storage represents an opportunity for basic and applied researchers to collectively overcome challenging scientific and technological barriers that directly address a critical societal and environmental necessity. In particular, development of high-energy-density batteries that are safe to operate could make a global electrified transportation industry a reality. Lithium battery technology is revolutionizing electrical energy storage; advances are recorded in periodic reviews.^{3–6} At present, however, state-of-the-art lithium-ion batteries, with a specific energy of $\sim 150 \text{ Wh kg}^{-1}$, do not yet have sufficient energy or life for use in electrified vehicles that would match the performance of internal combustion vehicles. Energy densities 2 and 5 times greater are required to meet the performance requirements of plug-in hybrid-electric vehicles (PHEVs) with a 40–80 mile all-electric range, and all-electric vehicles (EVs) with a 300–400 mile range, respectively. While the next generation of advanced lithium-ion batteries may approach the performance needed to satisfy the requirements of PHEVs, EVs will require new electrochemical couples such as lithium–sulfur or lithium–oxygen, which in principle offer at least five times the practical specific energy of present-day lithium-ion batteries.

This paper places lithium battery technology in a historical context, and it provides insights into how this technology might overcome the technological challenges facing electrically powered transportation.

2. Historical backdrop

Table 1 lists today's principal rechargeable battery systems of technological interest. The discovery of the first electrochemical cell is attributed to Alessandro Volta (1800) with his



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Table 1 Theoretical (Th.) and approximate practical (Pr.) specific (Sp.) energies of rechargeable batteries (theoretical values based on the masses of active electrode–electrolyte materials only; practical values based on mass of battery pack)^a

System	Negative electrode	Positive electrode	OCV ^b (V)	Th. Sp. Cap. (Ah kg ⁻¹)	Th. Sp. En. (Wh kg ⁻¹)	Pr. Sp. En. (Wh kg ⁻¹)
Lead–acid	Pb	PbO ₂	2.1	83	171	20–40
Ni–Cd	Cd	NiOOH	1.35	162	219	20–40
Ni–MH	MH alloy	NiOOH	1.35	~178	~240	50–70
Na–S (350 °C)	Na	S	2.1–1.78 (2.0)	377	754	~120
Na–MCl ₂ (300 °C)	Na	NiCl ₂	2.58	305	787	~90
Li-ion (1)	Li _x C ₆	Li _{1-x} CoO ₂ (layered)	4.2–3.0 (3.7)	158 (for x = 1.0)	584	100–150
Li-ion (2)	Li _x C ₆	Li _{1-x} Mn ₂ O ₄ (spinel)	4.2–3.0 (4.0)	104 (for x = 1.0)	424	80–100
Li-ion (3)	Li _x C ₆	Li _{1-x} FePO ₄ (olivine)	3.4 (3.4)	117 (for x = 1.0)	398	80–100
Li-ion (4)	Li ₄ Ti ₅ O ₁₂	Li _{1-x} Mn ₂ O ₄ (spinel)	2.5 (2.5)	80 (for x = 1.0)	200	50–70
Li-ion (5)	Li _x C ₆	Advanced spinel Li _{1-x} Mn _{1.5} Ni _{0.5} O ₄	4.7 (4.7)	105 (for x = 1.0)	493	Not yet commercialized
Li-ion (6)	Li _x C ₆	Advanced layered Li _{1-x} MO ₂ ^c	4.6–3.0 (3.7)	160 (for x = 1.0)	592	Not yet commercialized
Li-ion (7)	Li _y Si ^d (y _{max} ≈ 4.2)	Advanced layered Li _{1-x} MO ₂ ^c	4.0–2.5 (3.2)	263 (for x = 1.0)	843	Not yet commercialized
Li–polymer (80–120 °C)	Li	LiV ₃ O ₈	3.3–2.0 (2.6)	~340	~884	~150 (Removed from market because of fires)
Li–S	Li	S	~2.0	584	~1168	Not yet commercialized
Li–O ₂	Li	O ₂	~3.0	584 (Li ₂ O ₂), 897 (Li ₂ O)	~1752–2691	Not yet commercialized

^a This table lists specific (gravimetric) energy densities only (Wh kg⁻¹). Volumetric energy densities (Wh l⁻¹) are equally important, particularly for transportation applications, but are not provided here for brevity. ^b OCV = open circuit voltage. Average values are provided in parentheses. ^c e.g., LiMn_{0.67}Ni_{0.33}O₂ derived from 0.33Li₂MnO₃·0.67LiMn_{0.5}Ni_{0.5}O₂. ^d Li₃Si–carbon composite anodes are to be introduced by Panasonic in commercial Li-ion cells with conventional cathode materials in 2012.⁸

demonstration that two unlike metals, zinc and copper, when separated as electrodes (the anode and cathode, respectively) by an acidic electrolyte, produced an electric current by decomposing water and generating hydrogen. This discovery was followed a few decades later by Michael Faraday's major advances in developing the laws of electrochemistry, and the subsequent development of rechargeable batteries with aqueous electrolytes, notably lead–acid (Gaston Planté, 1859), nickel–cadmium (Waldemar Jungner, 1899), and nickel–iron (Thomas Edison, 1901) systems. A century ago, electric vehicles powered by lead–acid and nickel–iron batteries were much in vogue, in part due to Edison's passion for electric power and Henry Ford's interest, as reported in the *New York Times* on January 11th, 1914:⁹ “*Within a year, I hope, we shall begin the manufacture of an electric automobile. I don't like to talk about things which are a year ahead, but I am willing to tell you something of my plans. The fact is that Mr Edison and I have been working for some years on an electric automobile which would be cheap and practicable. Cars have been built for experimental purposes, and we are satisfied now that the way is clear to success. The problem so far has been to build a storage battery of light weight which would operate for long distances without recharging. Mr Edison has been experimenting with such a battery for some time.*” This first era of electric vehicles did not last long—it soon gave way to gasoline-powered automobiles. Nickel–cadmium and nickel–iron batteries were the forerunners of modern-day nickel–metal hydride batteries, introduced into the market in 1989, currently the system of choice for Toyota's hybrid-electric vehicle (HEV), the Prius. The low operating voltage of lead–acid and nickel-based batteries, a result of the low decomposition potential of water (~1.2 V) and the relatively heavy electrode components, compromises their practical energy (20–70 Wh kg⁻¹, Table 1) and, therefore, the electric range of an HEV or an EV.

In an HEV, the battery is used predominantly to save fuel during acceleration and to be charged through regenerative braking—a Prius can travel only 2–3 miles in all-electric mode. In a PHEV, such as the recently introduced Chevy Volt, the vehicle travels about 35 miles in all-electric mode before converting to gasoline as the source of power for driving the electric motor. The all-electric Nissan Leaf travels approximately 70 miles between charges.

Both the Chevy Volt and Nissan Leaf are electrically powered by lithium-ion batteries, a technology that had its roots in earlier non-aqueous battery research. The discovery in 1967 by researchers at the Ford Motor Company that the solid electrolyte “beta-Al₂O₃” (11Al₂O₃·xNa₂O) provided an anomalously high Na⁺ conductivity at elevated temperature^{10,11} and the oil crisis of the mid 1970s heralded the start of concerted international efforts to develop non-aqueous, high-temperature sodium batteries, which offered the promise of higher voltages and energy densities than room temperature batteries with aqueous electrolytes. Two sodium-based batteries that operate at 300–350 °C were subsequently commercialized: (1) Na–S (ref. 12) and (2) Na–NiCl₂ (ref. 13) (Table 1). While offering theoretical energy densities above 700 Wh kg⁻¹ (based on the mass of the active electrode and electrolyte materials only), these batteries are burdened by the additional weight and inconvenience of heating and cooling units to control both operating and standby temperatures and to avoid freeze-thaw cycling; in practice, they offer a specific energy between 120 and 90 Wh kg⁻¹, respectively.² Safety concerns about the possibility of a violent uncontained reaction between molten sodium and molten sulfur if the thin and fragile β-Al₂O₃ ceramic membrane were to rupture has rendered Na–S batteries unfavorable for mass transportation; they are being exploited predominantly for stationary, back-up energy storage. The Na–NiCl₂ (“Zebra”) battery employs a molten salt

NaAlCl₄ electrolyte that is reduced to Al metal and NaCl in the event of β-Al₂O₃ rupture, thereby enabling individual cells to fail safely in closed-circuit mode, but it is not immune to the possibility of sodium fires. At present, Na–NiCl₂ batteries are being marketed for stationary, back-up energy storage as well as niche mobile applications, such as demanding submarine applications (Rolls Royce), hybrid diesel–electric locomotives (General Electric), and bus fleets (Fiamm Sonik/MES-DEA).

Rechargeable, high-temperature lithium batteries with a design analogous to the sodium-based systems have not been exploited because of the lack of a suitable lithium-ion conducting ceramic electrolyte. Although an all-solid-state lithium metal/polymer electrolyte/LiV₃O₈ battery that operated at 80–120 °C was developed for stationary energy storage applications¹⁴ (Table 1), it was removed from the market because of fires that resulted from dendritic growth of lithium through the polymer membrane and consequent short circuits and internal heating. Recent renewed efforts indicate, however, that more stable polymer electrolytes and lithium metal phosphate cathodes¹⁵ may overcome the current safety limitations of all-solid-state lithium–polymer batteries that are being introduced into compact EVs, such as Bolloré's Bluecar.¹⁶ Short circuits and fires also occurred with room-temperature, rechargeable lithium metal/MoS₂ batteries in the late 1980s, leading to their early withdrawal from the market.¹⁷

The breakthrough in Li-ion battery technology occurred in 1991 with Sony Corporation's introduction of a high-voltage (~3.7 V) and high-energy Li_xC₆/non-aqueous liquid electrolyte/Li_{1-x}CoO₂ cell for portable electronic applications (Table 1). In this case, instead of using a metallic lithium anode, lithium is accommodated in a graphite host anode structure (denoted C₆ for convenience because the maximum uptake of Li by graphite is one lithium per graphene unit, LiC₆, at the top of charge), thereby avoiding dendrite formation, and in a LiCoO₂ cathode structure at the end of discharge. During charge and discharge, lithium ions shuttle reversibly between two host structures, hence the name *lithium-ion* cell (Fig. 1). Furthermore, the discovery of stable, liquid organic carbonate solvents allowed the reversible operation of these lithium-ion batteries at high voltage, at least up to 4.2 V. Since 1991, graphite has remained the anode material of choice, whereas several cathode materials have been implemented in commercial products, notably, compositional variations of layered LiCoO₂ with some Ni and Mn substituted for Co,¹⁸ stabilized LiMn₂O₄ (spinel),¹⁹ and LiFePO₄ (olivine)²⁰ (Table 1). In practice, blended cathodes are often used to improve cell performance and reduce cost.

3. Current lithium-ion batteries

Batteries discharge by dynamic electrochemical reactions that constitute a form of “inorganic life.” In their fully discharged state, batteries are “dead,” whereas when fully charged, the electrodes exist in a state far from thermodynamic equilibrium and can store massive amounts of potential energy. The release of electrical energy through an external electrical circuit has to be carefully controlled during discharge to drive electric motors and other devices without excessive heat generation; short circuits have to be avoided at all costs to avoid potentially catastrophic reactions and the risk of fire or explosion.

How Lithium-Ion Batteries Work

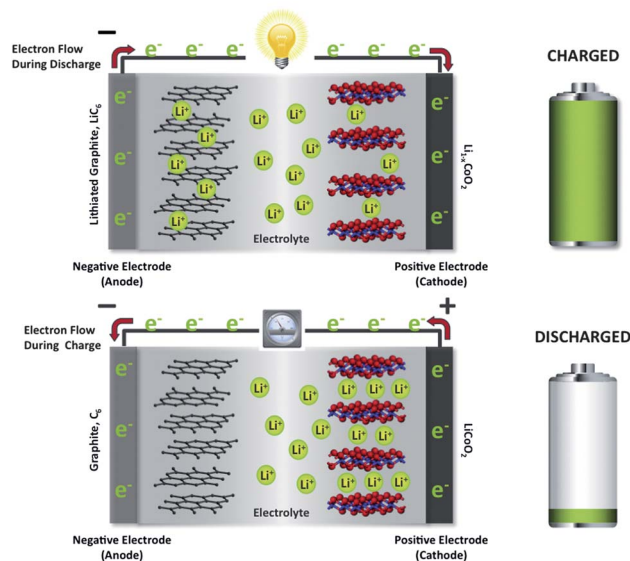


Fig. 1 A schematic illustration of the working principles of a Li_xC₆/Li_{1-x}CoO₂ lithium-ion cell. During discharge, lithium ions diffuse from a lithiated graphite (Li_xC₆) structure (the anode) into a delithiated Li_{1-x}CoO₂ structure (the cathode) with concomitant oxidation and reduction of the two electrodes, respectively. The reverse process occurs during charge.

Lithium is the third lightest element and has the highest oxidation potential of all known elements (3 V above the standard hydrogen potential). It is, therefore, not surprising that lithium batteries offer the best prospects for developing high energy and high power batteries to satisfy the future needs of an electrified transportation industry (Fig. 2). While lithium-ion batteries hold the best short-to-medium term prospects for improvement, the practical electrochemical capacities of a graphitic anode (LiC₆, 300–350 mAh g⁻¹) and commercialized cathode materials (layered LiMO₂, M = Co, Ni, Mn, 140–160 mAh g⁻¹; spinel LiMn₂O₄, 100–120 mAh g⁻¹; and olivine LiFePO₄, 140–160 mAh g⁻¹) still fall far short of the long-term goals for PHEV and EV batteries. Lithium-ion battery products with a carbon anode and a blend of stabilized layered LiMO₂ and spinel LiMn₂O₄ materials as the cathode are used in the first-generation Chevy Volt (PHEV) and in the Nissan Leaf (EV). Lithium-ion batteries are also being introduced by Toyota for their next generation HEVs. In addition, to enhance safety, 2.5 V high-power lithium-ion batteries containing a lithium titanate spinel anode, Li₄Ti₅O₁₂, which operates 1.5 V above the potential of metallic lithium, and a spinel cathode, LiMn₂O₄, are being marketed for HEVs and compact EVs.²¹ The Li₄Ti₅O₁₂ spinel has approximately half the theoretical capacity of a graphite anode (372 mAh g⁻¹), so Li₄Ti₅O₁₂/LiMn₂O₄ cells offer a low theoretical specific energy, 200 Wh kg⁻¹, relative to conventional Li-ion batteries; this specific energy is similar to that offered by Ni–MH batteries (Table 1). Lithium-ion batteries with Li₄Ti₅O₁₂ anodes are, therefore, more likely to be used in the long term for stationary energy storage and niche markets, such as HEVs, in the transportation sector.

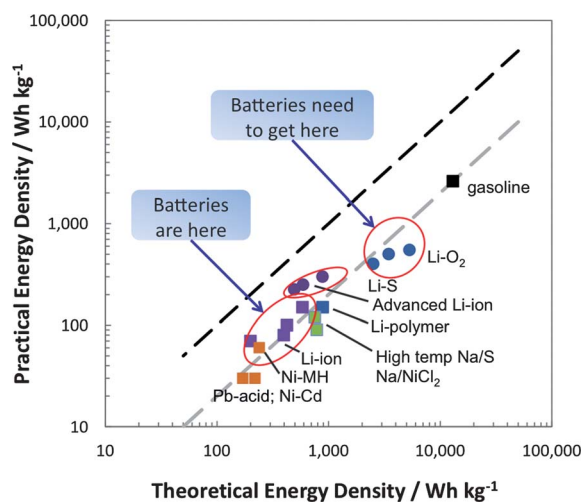


Fig. 2 A plot of the theoretical specific energy of various rechargeable battery systems vs. their practical specific energies, illustrating the enormous challenge of increasing the practical energy density of today's batteries toward the energy stored and delivered by gasoline.

Advances in anode and cathode materials development are anticipated, at best, to double the practical specific energy of lithium-ion battery packs ($\sim 300 \text{ Wh kg}^{-1}$). Clearly, alternative approaches are required to move energy storage “beyond lithium ion.” On paper, lithium–oxygen (ultimately lithium–air) and lithium–sulfur systems appear to offer the greatest hope for the future: theoretical specific energies 2–4 times greater than lithium-ion systems (Table 1). The use of room-temperature sodium^{22,23} or multi-valent cation²⁴ systems instead of lithium, or extensions of the aqueous vanadium oxide redox flow system²⁵ to higher voltage, non-aqueous systems are being proposed by the academic community and start-up companies, but these ideas and systems do not yet have traction and are not discussed here.

4. Next generation lithium-ion batteries—approaching the practical limit

The mechanism by which conventional lithium-ion batteries function, *i.e.*, the insertion and removal of lithium from anode and cathode host structures (Fig. 1), particularly those that operate at high voltages, challenges the structural integrity and chemical stability of electrodes when continually exposed to extremely low and high electrochemical potentials vs. lithium, respectively, thereby degrading both operational and calendar life. Furthermore, the non-aqueous electrolytes of choice contain corrosive fluorinated salts, such as LiPF_6 , and flammable organic solvents, such as ethylene carbonate and dimethyl carbonate, that are only stable to approximately 4.2 V vs. lithium. Lithium-ion batteries in their charged state, particularly those with delithiated metal oxide cathodes, such as $\text{Li}_{1-x}\text{CoO}_2$, are intrinsically unsafe. To circumvent the possibility of thermal runaway and fire, the battery must be designed to avoid the reaction of oxygen, released from a strongly oxidizing cathode, with a strongly reducing lithiated graphite anode that operates close to the potential of metallic lithium, in the presence of a flammable electrolyte, despite the spontaneous formation of a protective solid-electrolyte interphase (“SEI layer”) at the

Li_xC_6 –electrolyte interface.¹ To improve the electrode surface stability, and hence the safety and longevity of lithium-ion cells, significant improvements are needed to protect anode and cathode surfaces and to deactivate the electrode–electrolyte interface with thin lithium-ion conducting films and architectures. At the same time, there is an urgent need to find alternative non-flammable electrolytes that are stable over wider operating voltage windows.

Increasing the specific energy of lithium-ion cells requires anode and cathode materials with higher capacity and/or cell voltage. [Note: specific energy = $V \times It$ (Wh kg^{-1}), where V is the cell voltage (V), and It (Ah kg^{-1}) the electrochemical capacity of the cell (in coulombs kg^{-1} of anode and cathode material, disregarding the mass of the other components in the cell for simplicity—see Table 1).] In this respect, several approaches are being adopted in attempts to enhance the performance of state-of-the-art lithium-ion batteries.

4.1. High potential cathodes—Spinel $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and olivine LiMPO_4

Spinel LiMn_2O_4 electrodes require stabilization with a few percent of substituent ions (*e.g.*, lithium and aluminium for manganese) to reduce manganese solubility in the electrolyte, which is associated with a high concentration of Mn^{3+} ions in the parent LiMn_2O_4 electrode structure and a consequent loss of cell capacity on long-term cycling;¹⁹ the Mn^{4+} – Mn^{3+} couple offers an electrochemical potential of approximately 4.0 V vs. metallic Li. In contrast, a nickel-substituted $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel cathode offers 4.7 V;²⁶ in this case, the electrochemical potential is derived from a Ni^{4+} – Ni^{2+} couple, the Mn^{4+} ions acting as inactive spectator ions and reducing manganese solubility.²⁷ $\text{Li}_x\text{C}_6/\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cells offer a theoretical specific energy of 493 Wh kg^{-1} , which is 16% higher than that of conventional $\text{Li}_x\text{C}_6/\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ spinel cells (424 Wh kg^{-1} , Table 1). Despite offering superior energy, the higher voltage $\text{Li}_x\text{C}_6/\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cells currently suffer from operational instabilities that are more noticeable at elevated temperatures (*e.g.*, 55 °C). The deterioration of cell performance above room temperature is attributed predominantly to electrolyte–electrode reactions at 4.7 V (or higher on charge), stressing the need to find more stable (and non-flammable) electrolyte systems.

Attempts to replace LiFePO_4 (3.4 V) by high potential, lithium-metal-phosphates with the olivine structure, such as LiMnPO_4 (4.1 V), LiCoPO_4 (4.8 V), and LiNiPO_4 (5.2 V) have, to date, also been unsuccessful, although some promise has been shown by the solid solution system $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$, which operates by two distinct processes between 4.1 and 3.5 V.²⁸

4.2. High capacity cathodes from $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ precursor

Li_2MnO_3 -stabilized LiMO_2 ($M = \text{Mn, Ni, Co}$) electrodes with highly complex “composite” layered-type structures, derived from a $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Mn, Ni, Co}$) precursor, form an intriguing family of compounds.²⁹ They can deliver all their theoretical electrode capacity ($\sim 260 \text{ mAh g}^{-1}$), based on the formal redox reactions of the transition metal ions, in contrast to commercial layered LiMO_2 ($M = \text{Mn, Ni, Co}$) electrodes, such

as LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, and $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, which offer only 50–60% of their full capacity (140–170 mAh g^{-1}); stabilized LiMn_2O_4 (spinel) and LiFePO_4 (olivine) cathodes offer at best between 120 and 170 mAh g^{-1} of capacity, respectively. Li_2MnO_3 -stabilized LiMO_2 materials were discovered during early attempts to synthesize a layered MnO_2 structure by leaching Li_2O from Li_2MnO_3 ($\text{Li}_2\text{O} \cdot \text{MnO}_2$) in acid.^{30,31} After relithiation in an electrochemical cell, the resulting compound had the formula $\text{Li}_{1.09}\text{Mn}_{0.91}\text{O}_2$ or, in two-component “composite” notation, $0.2\text{Li}_2\text{MnO}_3 \cdot 0.8\text{LiMnO}_2$; such Li_2MnO_3 -stabilized LiMnO_2 electrodes are more stable to electrochemical cycling and resistant to transformation to a spinel-type structure than a pure layered LiMnO_2 electrode.³² Significant improvements in the electrochemical stability and capacity of these electrode materials were subsequently made by introducing nickel, in particular, for manganese in the LiMnO_2 component,^{7,33} for example, $0.33\text{Li}_2\text{MnO}_3 \cdot 0.67\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$.⁷ Capacities approaching 300 mAh g^{-1} , which exceed the theoretical limit imposed by the formal redox reactions of the transition metal ions in $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ electrodes, have been observed—particularly when cells are operated at low current rate and at elevated temperature, typically $\sim 50^\circ\text{C}$.^{34–36} Although the anomalous additional capacity is not yet understood, it has been speculated to result from the participation of the oxygen ions in the electrochemical reaction or by accessing a manganese oxidation state above 4+.³⁴

The operating principle of Li_2MnO_3 -stabilized LiMO_2 electrodes is shown in Fig. 3 with specific reference to two starting compositions, namely, $0.05\text{Li}_2\text{MnO}_3 \cdot 0.95\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $0.33\text{Li}_2\text{MnO}_3 \cdot 0.67\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$. When charged and discharged between 4.3 and 3.0 V, the typical voltage range of a commercial lithium-ion cell, the Li_2MnO_3 component stabilizes the electrochemically active $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ component and does not participate in the reaction, resulting in capacities of 160–170 mAh g^{-1} . Electrodes of this type are often blended with a stabilized LiMn_2O_4 spinel component; they are being used in the first generation of lithium-ion batteries for the Chevy Volt. If,

however, the Li_2MnO_3 content is increased to 33% and the voltage increased to 4.6 V, the initial charge and discharge reaction follows the dashed blue line in Fig. 3.⁷ During charge to 4.5 V, lithium is first extracted from the $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ component until the Li_2MnO_3 – MO_2 tie-line is reached, when the electrode composition is $0.33\text{Li}_2\text{MnO}_3 \cdot 0.67\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$. Thereafter, lithium is extracted from the Li_2MnO_3 ($\text{Li}_2\text{O} \cdot \text{MnO}_2$) component with the concomitant loss of oxygen (net loss Li_2O), creating a MnO_2 component that remains integrated with the $\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ matrix of the parent $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ component; some, but not all, of the lost oxygen has been observed as O_2 gas.³⁷ This is a remarkable reaction because the removal of both lithium and oxygen does not destroy the overall layered character of the structure, nor its crystallinity. Essentially all the lithium can be removed from these manganese-rich composite structures, such that the theoretical capacity can be delivered by the electrochemically activated electrode ($0.33\text{MnO}_2 \cdot 0.67\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ or, alternatively, $\text{Mn}_{0.67}\text{Ni}_{0.33}\text{O}_2$) because tetravalent manganese is significantly more stable than tetravalent nickel (and cobalt) at 4.6 V. In practice, it is believed to be beneficial to keep a small amount of Li_2MnO_3 within the cathode structure to maintain electrochemical and structural stability at the higher cell voltages. These high-capacity lithium- and manganese-rich electrode materials cannot be synthesized in their lithiated state; at present, the only known route is through *in situ* electrochemical activation and the subsequent discharge process, described above and shown in Fig. 3.

Despite these promising developments, high-capacity $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ electrodes suffer for a number of reasons from performance limitations that are slowing their entry into the next generation of lithium-ion battery products for vehicle propulsion: (1) the rate (power) capability of the electrode is limited by the electrochemical activation process (Li_2O removal) at 4.6 V, which damages the surface of the electrode particles;³⁸ (2) activated electrodes undergo a voltage decay associated with internal phase transitions on cycling, which lowers the energy output and energy efficiency of the cell;³⁹ and (3) a charging voltage of 4.6 V is above the stability threshold of known electrolytes, thereby leading to electrode–electrolyte decomposition and capacity fade. Nevertheless, because these layered composite metal oxide cathodes can provide a capacity almost twice that of conventional layered, spinel, and olivine cathodes (Table 1), a concerted international effort is underway to find solutions to their performance limitations.

Doubling the Capacity of Li-ion Cathodes

Li_2O is removed from the Li_2MnO_3 component at high potentials (>4.5 V)

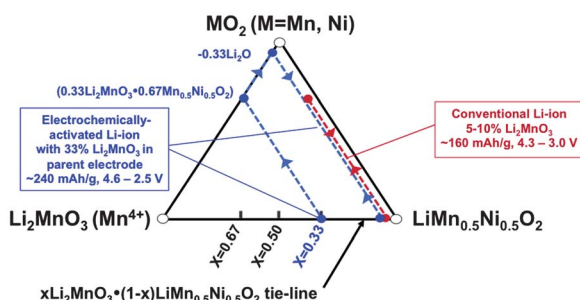


Fig. 3 A schematic compositional phase diagram illustrating the charge and discharge reaction pathways of a conventional lithium-manganese-nickel-oxide cathode with a capacity of approximately 160 mAh g^{-1} (dashed red line) for a lithium-ion battery and one that requires electrochemical activation above 4.5 V that provides a significantly higher capacity (~ 240 mAh g^{-1}) and consequently a higher cell energy.⁷

4.3. Silicon anodes

Despite graphite, C_6 , being the anode material of choice for today's lithium-ion batteries, it can accommodate only one lithium atom per graphene unit, thereby compromising its theoretical electrochemical capacity (372 mAh g^{-1}). Worldwide efforts are, therefore, underway to find higher capacity anode materials that can be coupled with high capacity cathode materials, such as those mentioned above. Metals and metalloids, such as Sn and Si, can accommodate more than four lithium atoms per metal/metalloid unit, providing theoretical capacities of 960 and 4009 mAh g^{-1} , when lithiated to the compositions $\text{Li}_{17}\text{Sn}_4$ ($\text{Li}_{4.25}\text{Sn}$) and $\text{Li}_{21}\text{Si}_5$ ($\text{Li}_{4.20}\text{Si}$), respectively.⁴⁰ The latter composition offers more than 10 times the capacity of graphite at

approximately 500 to 10 mV above the potential of metallic lithium in a practical cell.⁴¹ For example, the theoretical capacity of a balanced $\text{Li}_{4.2}\text{Si}$ /high capacity, lithium-metal-oxide cathode cell offers a theoretical energy density of 843 Wh kg^{-1} , *i.e.*, 44% more than conventional LiC_6 /layered $\text{Li}_{1-x}\text{MO}_2$ cells (584 Wh kg^{-1} , Table 1). However, metals and metalloids have densely packed structures and, therefore, expand and contract many-fold during lithiation and delithiation reactions (charge and discharge, respectively). This volumetric expansion leads to pulverization and amorphization of the electrode particles, which severely compromise the maintenance of electronic conductivity and cycle life. For instance, bulk silicon experiences a volume expansion of $\sim 400\%$ when lithiated to full capacity.⁴² Recent efforts have focused largely on designing and controlling Si electrodes because of their extremely attractive specific and volumetric capacity relative to other anode materials. Encouraging results have been achieved by clever materials engineering: for example, (1) crystallographic alignment of silicon rods by lithographic patterning to take advantage of their anisotropic expansion to mitigate volumetric expansion and enhance cycling stability,⁴² or (2) dispersion of silicon nanoparticles in graphene architectures⁴³ or electronically conductive binders⁴⁴ to accommodate the volumetric expansion of the nanoparticles and maintain electronic conductivity between them. A recent announcement from Envia Systems boasts the successful development of a lithium-ion cell (not yet commercialized) with an energy density of 400 Wh kg^{-1} (at the cell, not battery pack, level) using a Si-C composite anode coupled to a high-capacity, lithium-metal-oxide cathode.⁴⁵ This value is 47% of the theoretical 843 Wh kg^{-1} offered by a $\text{Li}_y\text{Si}/\text{Li}_{1-x}\text{MO}_2$ ($\text{M} = \text{Mn, Ni, Co}$; $y_{\text{max}} = 4.2$; $0 \leq x \leq 1$) electrochemical couple (Table 1).

5. Going beyond Li ion—batteries with metal lithium anodes

From the foregoing discussion, it is abundantly clear that lithium-ion technologies, even those being proposed for the next generation of battery products, do not yet meet the long-term performance targets for all-electric vehicles. Materials and processing costs, performance limitations, and the uncertainties of new, insufficiently validated electrochemical couples and materials in a rapidly maturing market are all factors that indicate that progress in lithium-ion battery technology is likely to be incremental rather than exponential. The best opportunity for greater than incremental advances appears to lie in systems that use metallic lithium as the anode, coupled to a cathode that is significantly lighter than the metal oxide or metal phosphate electrodes in Table 1. Scanning the periodic table for potentially useful electronegative elements, it is logical to select sulfur and oxygen as attractive candidate cathode materials, fluorine gas being too corrosive as a viable option despite its extremely high potential against lithium ($\sim 6 \text{ V}$).

The chemical, electrochemical, and engineering challenges of lithium-sulfur and lithium-oxygen electrochemical couples have recently been reviewed by Bruce *et al.*⁴⁶ and Christensen *et al.*⁴⁷ Unlike lithium-ion systems that operate by lithium intercalation reactions, lithium-sulfur and lithium-oxygen reactions occur by conversion reactions at the electrode surface to form lithium

polysulfide and lithium oxide products, respectively. Both systems suffer from the potential safety hazards of (1) lithium dendrite formation, which can lead to short circuits and to rapid, uncontrolled discharge, and (2) sulfur or oxygen crossover that poisons/passivates the lithium electrode and leads to cycling inefficiencies and a general degradation of cell performance. Despite their poor cycle life, energy densities of 350 Wh kg^{-1} have been reported for prototype Li-S cells, with an improvement to 600 Wh kg^{-1} anticipated.⁴⁶ Sion Power has developed Li-sulfur batteries for unmanned aerial vehicles (*e.g.*, drones) that presumably do not require a long cycle life;⁴⁸ significant advances are certainly required before these batteries can be considered for PHEVs or EVs.

The lithium-oxygen system can be considered the “holy grail” of lithium batteries (Fig. 4). Strictly speaking, with a solid lithium anode and oxygen gas as the cathode, it can be considered a battery/fuel cell hybrid. At this stage of its development, lithium-oxygen cells, and even more so lithium-air cells, are severely compromised by the limitations of the metallic lithium and oxygen electrodes. Despite extremely challenging obstacles, the difficulties of overcoming them and the risk of failure are likely to be countered by a science-rich investment. Continued research is likely to spawn the discovery of new electrode, electrocatalyst, and electrolyte systems and breakthrough solutions that are also likely to spin off advances in lithium-ion battery technologies.

A lithium-oxygen cell offers a theoretical specific energy of 1752 Wh kg^{-1} if the oxygen electrode is discharged to lithium peroxide, Li_2O_2 , *i.e.*, without severing the oxygen-oxygen bond. This reaction is reversible if side reactions with the electrolyte solvents can be avoided. In particular, carbonate-based electrolyte solvents, such as propylene carbonate or those used in commercial lithium-ion batteries, are considered notoriously reactive in Li-oxygen cells;⁴⁶ these reactions form solid carbonate

Beyond Lithium-Ion: Li-O₂?

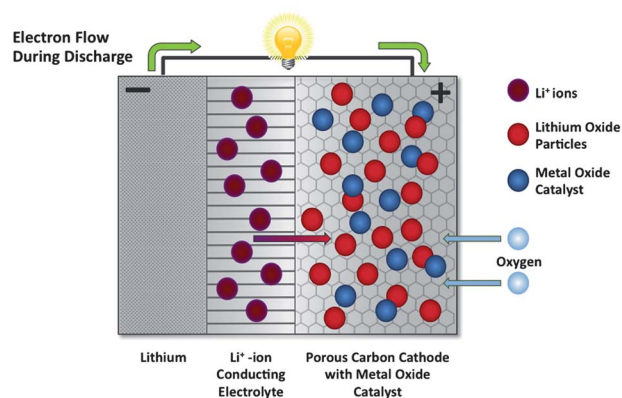


Fig. 4 A schematic illustration of a high-energy-density Li-O₂ cell, in which lithium reacts with oxygen to form lithium oxide products on the surface of carbon and metal oxide electrocatalysts. Significant challenges are to overcome the limitations of safety, extremely slow charge and discharge rates, poor energy efficiency (high polarization), and a limited cycle life.

products that can clog the pores of the oxygen electrode and dry out the electrolyte on cycling, causing rapid cell degradation. Although progress has been made with more promising electrolyte solvents, such as ether-based⁴⁹ systems including silanes,⁵⁰ these advances do not yet overcome significant polarization effects, cycling inefficiencies and instabilities, and rate limitations during long-term discharge and charge. Discharge of lithium–oxygen cells to Li_2O , which has an antifluorite-type structure, would increase the theoretical specific energy to an extremely high 2691 Wh kg^{-1} (Table 1), but it destroys the oxygen–oxygen bond, severely limiting the ability to recharge the cell. Some sign of success has been shown by a recent intuitive approach that uses transition metal oxides such as activated Fe_2O_3 and MnO_2 as electrodes/electrocatalysts, which have a strong affinity to form compounds with Li_2O , such as Li_5FeO_4 ($5\text{Li}_2\text{O}\cdot\text{Fe}_2\text{O}_3$) with a defect antifluorite-type structure ($\text{Li}_{1.25}\text{Fe}_{0.25}\square_{0.5}\text{O}$).⁵¹ It has been demonstrated, in particular, that lithium and oxygen can be removed electrochemically from Li_5FeO_4 , corresponding to 4 Li_2O units from 5 $\text{Li}_2\text{O}\cdot\text{Fe}_2\text{O}_3$, in two steps between 3.5 V and 4.0 V,⁵² which is considerably lower than the anticipated potential to decompose pure Li_2O into its constituent elements. Unlike lithium–oxygen cells that contain only carbon as electrocatalyst, those with activated $\alpha\text{-MnO}_2$ electrocatalysts, produced by leaching the Li_2O component from Li_2MnO_3 ($\text{Li}_2\text{O}\cdot\text{MnO}_2$), can increase the delivered capacity of the oxygen electrode to 5000 mAh g^{-1} ,⁵³ at least for a few cycles. These results provide hope for combating at least one of the major challenges holding back advances in rechargeable lithium–oxygen battery technology.

6. The power of computing: battery materials by design

The development of new battery materials and technologies has relied on a detailed, fundamental understanding of materials properties at an atomistic level. On this scale, powerful quantum computational techniques, such as density functional theory (DFT), can be utilized to predict many material properties.⁵⁴ Computational materials science can extend research into spatial and temporal territories where physical experimentation and observation become very limited, thus accelerating the discovery of safe electrode materials with high energy density. Computation has traditionally been critical in aiding our understanding of experiment or proving or disproving hypotheses. High performance computing capabilities together with the modeling and simulation tools developed to utilize this computing power are now enabling us to make predictions regarding regions of materials and chemistries that are difficult to obtain experimentally, for instance, harsh or toxic environments, exactly those environments in which batteries operate.

The application of DFT to Li-ion battery materials goes back to the 1990s.^{55–58} These initial studies mostly focused on the computation of voltages of various cathode and anode materials. Over the past two decades, the use of DFT has become widespread and has been applied to a variety of materials properties, such as voltage, crystal structure, Li diffusion, electronic properties, and reactivity.⁵⁹

The modern use of DFT has evolved beyond merely trying to explain the properties of experimentally investigated materials.

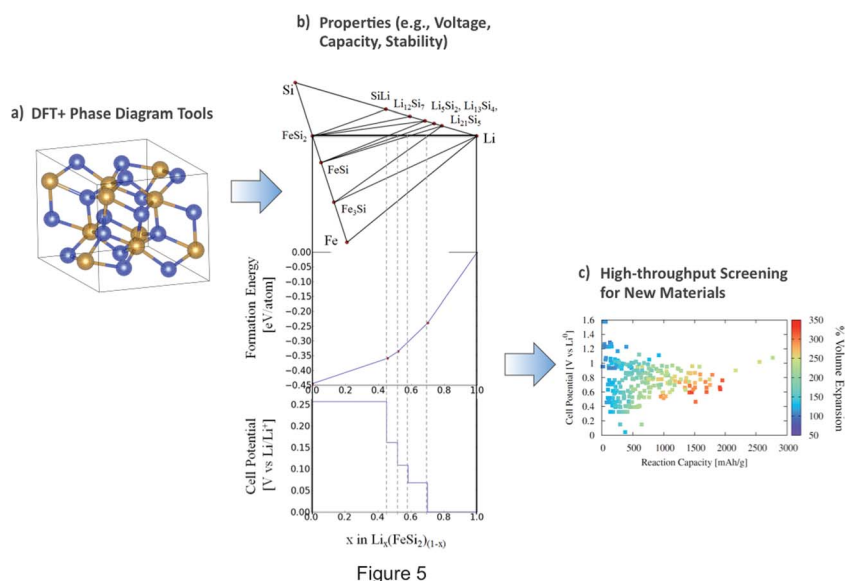


Figure 5

Fig. 5 Schematic illustration of the use of computation to accelerate the materials discovery and development process. (a) The left panel illustrates density functional theory (DFT), which provides an atomic-scale description of many material properties. (b) The middle panel illustrates (for FeSi_2 as a conversion reaction anode) how DFT and phase stability tools may be used to compute properties of lithiation reactions, such as voltages, energy density, and volumetric expansion. On the ternary phase diagram, the lithiation reactions change upon crossing any intersecting tie-line, and form a kink in the energy vs. composition “convex hull”. The voltage as a function of composition is simply the slope of each segment of the convex hull; therefore, the voltage–capacity curve will have a step at each kink in the convex hull. (c) The right panel illustrates how these properties may be collected for a large number of materials and used to effectively “screen” materials to predict new sets of materials with desired properties. These predicted sets would then be passed on for experimental testing or validation, which would provide useful feedback to computation to further refine the screening process.

Advances in computer algorithms and hardware over the past decades have made it possible to use “high-throughput” DFT, where computations are performed for hundreds or thousands of materials (many of which may have never been synthesized in a laboratory) in an effort to predict and design new materials and compounds. High-throughput DFT computation has become a tool used to predict properties of many material classes, such as structural metal alloys, catalysts, and Li-ion battery materials.^{60–63} This approach has been adopted for screening new cathode materials for lithium batteries^{64,65} and, most recently, for predicting new anode displacement reactions.⁶⁶

Moreover, the discovery of new materials for batteries, or any other desired outcome in new energy or other technologies for that matter, is just recently beginning to involve strongly integrated use of computational tools with experimental efforts in an iterative manner, illustrated in Fig. 5.⁶⁶ DFT and other computational methods can be used to screen for sets of materials with desired attributes. These predicted sets would then be passed on for experimental testing or validation. The experimental results would consequently provide useful feedback to computation to further refine the screening process. Although the accuracy of these predictions must be validated against measured data, this iterative approach seems destined to guide and accelerate discovery of new materials compared to purely Edisonian methods. Successful computationally aided discovery and understanding would, of course, be particularly opportune for immature systems such as Li–O₂ and Li–sulfur with their wide-ranging materials challenges and barriers involving electrodes, electrolytes, interfaces, and additive materials, which could have a profound effect on stabilizing electrode–electrolyte interactions.⁶⁷

7. Concluding remarks

Revolutionizing the transportation market by electrification and transforming the energy grid by widespread adoption of renewable energy sources will require innovative new ideas for energy storage systems. Major breakthroughs, and not incremental advances, in materials and chemistries are required. Lithium-based systems provide considerable headroom for improved energy densities; factors of two to three are achievable for Li-ion systems, and factors of five or more may be possible for Li–oxygen systems. The challenge will be to achieve real scientific and technological breakthroughs in material discoveries in order to provide control of electrode materials that exist and operate far away from equilibrium, particularly in their charged state; accommodate large volumetric and/or structural changes over many charge–discharge cycles; and can simultaneously support multiple functions—for instance, development of an oxygen cathode that can be reduced to Li₂O and, at the same time, provide a catalyst that can readily break the Li–O bonds when recharging the battery. Electrolytes also offer tremendous opportunities for innovative research to find systems that are stable in a working environment over a wide voltage window; in particular, finding a stable, non-volatile, non-aqueous electrolyte solvent for Li–oxygen systems remains an enormous challenge. At the same time, if the storage system is to be widely adopted, science will have to provide the materials that can deliver improved electrochemical performance, safety and cost.

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