

# Rechargeable lithium batteries and beyond: Progress, challenges, and future directions

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This issue contains assessments of battery performance involving complex, interrelated physical and chemical processes between electrode materials and electrolytes. Transformational changes in battery technologies are critically needed to enable the effective use of renewable energy sources such as solar and wind to allow for the expansion of hybrid electric vehicles (HEVs) to plug-in HEVs and pure-electric vehicles. For these applications, batteries must store more energy per unit volume and weight, and they must be capable of undergoing many thousands of charge-discharge cycles. The articles in this theme issue present details of several growing interest areas, including high-energy cathode and anode materials for rechargeable Li-ion batteries and challenges of Li metal as an anode material for Li batteries. They also address the recent progress in systems beyond Li ion, including Li-S and Li-air batteries, which represent possible next-generation batteries for electrical vehicles. One article reviews the recent understanding and new strategies and materials for rechargeable Mg batteries. The knowledge presented in these articles is anticipated to catalyze the design of new multifunctional materials that can be tailored to provide the optimal performance required for future electrical energy storage applications.

## Introduction

Energy based on electricity generated from renewable sources, such as solar or wind, offers enormous potential for meeting the growing demand for energy with low or even zero emission, considering that world energy consumption within the next 50 years could be doubled at least (see the April 2008 issue of *MRS Bulletin*, “Harnessing Materials for Energy”). However, the utilization of electricity generated from these intermittent renewable sources requires efficient electrical energy storage (EES) systems. Batteries, as one of the most appropriate and promising EES systems, are ubiquitous—virtually all portable electronic devices today rely on the chemical energy stored in them. There is no doubt that the development of the next generation of batteries will play a vital role in future use of electrical energy.

A rechargeable Li-ion battery consists of two Li-ion intercalation electrodes with a non-aqueous electrolyte in between for ionic conduction. The electrical and chemical energies in a Li-ion cell are interconverted via reversible de-intercalation/intercalation processes of Li ions between the cathode

and anode along with electrons traveling via an external circuit simultaneously. The advent of rechargeable Li-ion batteries ushered in the wireless revolution and has stimulated a quest for batteries to power hybrid electric vehicles (HEVs) and pure electric vehicles (PEVs).<sup>1</sup> Lithium batteries are also anticipated to be a key component to realize the full potential of renewable energy sources as part of the electrical distribution grid.<sup>2</sup> Another motivation to discover novel EES systems, in particular rechargeable Li batteries with new chemistries, is the ceaseless fluctuation of fossil fuel prices and the prospect of global warming associated with CO<sub>2</sub> emission. The deployment of the rechargeable lithium batteries will reduce fossil fuel usage and hence reduce CO<sub>2</sub> emissions.

The cost and performance limitations of existing Li-ion battery technologies seriously hinder the rapid transition to EVs and efficient use of renewable energy sources. Other technical bottlenecks of Li-ion batteries should also be considered, including the limited energy density of individual cells, the lack of fast recharge cycles with long cell lifetimes, as well as safety concerns. In order to increase the energy density of

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individual cells significantly, one can either increase the cell voltage and/or the amount of charge stored reversibly per unit weight and volume. One approach that can increase the cell voltage is to develop novel cathode materials, for example 5V spinel ( $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ).<sup>3</sup> However, enabling cell performance with high voltages requires developing new electrolytes and/or electrolyte additives for thermodynamic stability or novel surface passivation layers that adjust rapidly to changes in electrode morphology during a fast charge and discharge process. Increasing the amount of charge stored reversibly may require identifying new redox couples in the host electrode materials that could accept more than one electron at a time over a small voltage window. Reversible magnesium batteries are an example.<sup>4</sup>

Exploring new electrochemistries beyond the intercalated Li-ion couples could also enhance the amount of charge stored in the cell (e.g., Li-S and Li-air batteries).<sup>5,6</sup> Furthermore, exploration of new materials that have nanoscale features could enhance reversible charge storage, considering the need to mitigate the volume and structural changes in the active electrode in a charge-discharge cycle.<sup>7</sup> This is extremely important for electrode materials that show large volume change during the cycle, for example, Si-based anode materials.<sup>8</sup> Especially exciting is the potential for designing novel multifunctional materials that could increase the level of energy storage per unit volume and decrease dead weight (the weight of electrochemically inactive materials).<sup>9</sup>

This overview article briefly describes rechargeable Li batteries related to their applications in current and future electrical vehicles as well as grid energy storage. We describe some of the history and evolution of rechargeable Li-ion batteries and discuss in some detail newer cathode materials with much higher energy densities. The progress and challenges of high-capacity anode materials, especially Si-based anodes, as well as the protection of Li metal as an anode material are also briefly discussed. An overview of Li electrochemistry beyond the conventional intercalated Li-ion battery is presented in the section on Li-ion systems. These “beyond Li-ion” systems include Li-S, Li-air, and Mg batteries. We also present prospects for future development of rechargeable Li batteries.

The goal of this article is to familiarize readers with the frontiers of research in Li electrochemistry and to evaluate and summarize progress and challenges at hand, which can advance future R&D of rechargeable Li batteries.

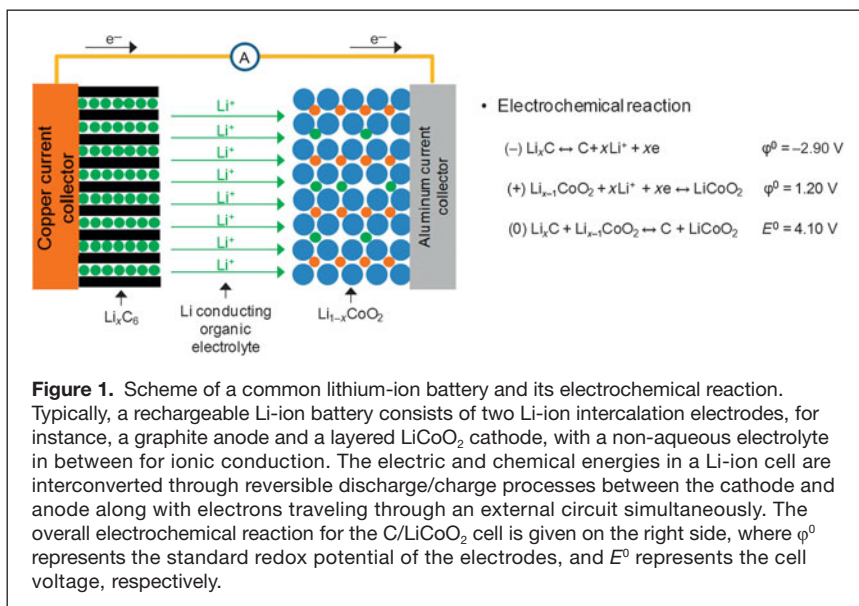
### Rechargeable Li-ion batteries

The introduction of non-aqueous rechargeable Li-ion batteries in the 1970s and the commercialization in the 1990s to power portable electronic devices, such as cellular phones and laptop computers, sparked a revolution in

battery technology. This marked a massive swing away from the relatively low-voltage, water-based systems such as Ni-Cd and nickel metal hydride (NiMH) batteries as well as high-temperature systems, such as conventional Na-S batteries. Nowadays, rechargeable Li-ion batteries are being pursued intensively for a myriad of devices, such as uninterrupted power supply units, rechargeable power sources for consumer electronics, and electrical vehicles.

The first commercial Li-ion battery, introduced by Sony Corporation in 1991, was based on a  $\text{LiCoO}_2$  cathode and a carbon anode, as schematically shown in **Figure 1**. When an electrical current is applied to charge the cell, lithium ions move out of the cathode ( $\text{Li}_{1-x}\text{CoO}_2$ ) and become trapped inside the anode storage medium, which is usually graphitized carbon ( $\text{Li}_x\text{C}_6$ ). Upon battery discharge, the lithium ions travel back to the cathode and produce an external electrical current. During cell operation at 3.0–4.2 V, however, the surface reactivity and instability of the delithiated  $\text{Li}_{1-x}\text{CoO}_2$  structure limit the practical capacity of the  $\text{LiCoO}_2$  electrodes to approximately 140 mAh/g, which corresponds to  $x \approx 0.5$  (i.e., ~50% of its theoretical value [273 mAh/g]).<sup>10</sup> These limitations, together with the high possibility of thermal runaway caused by cell overcharge and short circuit in inadequately controlled batteries and the relatively high cost of cobalt, have led to enormous efforts since 1991 to find alternative cathode materials to  $\text{LiCoO}_2$  that provide Li-ion cells with superior energy density, rate capability, safety, and cycle life.

Insertion electrodes for Li-ion electrochemical cells need to have stable structures over a wide compositional range such that as much lithium as possible can be extracted and reinserted during repeated charging and discharging to maximize cell energy density and cycle life.<sup>1</sup> Furthermore, the host structures must have interstitial spaces that provide energetically favorable pathways for fast Li-ion transport—that is, high power capability. Since carbon in the form of graphite is the material



**Figure 1.** Scheme of a common lithium-ion battery and its electrochemical reaction. Typically, a rechargeable Li-ion battery consists of two Li-ion intercalation electrodes, for instance, a graphite anode and a layered  $\text{LiCoO}_2$  cathode, with a non-aqueous electrolyte in between for ionic conduction. The electric and chemical energies in a Li-ion cell are interconverted through reversible discharge/charge processes between the cathode and anode along with electrons traveling through an external circuit simultaneously. The overall electrochemical reaction for the C/ $\text{LiCoO}_2$  cell is given on the right side, where  $\phi^0$  represents the standard redox potential of the electrodes, and  $E^0$  represents the cell voltage, respectively.

of choice for the anode for the Li-ion battery industry, these requirements must be achieved by varying the cathode materials. Incidentally, the nearly universal use of graphite anodes also explains why battery cell characteristics can be discussed in terms of the cathode's properties alone.

Several alternative cathode materials to  $\text{LiCoO}_2$  have been exploited by the Li-ion battery industry over the past decade. They include compositional variations of the layered  $\text{LiCoO}_2$  structure, such as  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA);<sup>11</sup> spinel electrodes derived from  $\text{LiMn}_2\text{O}_4$ , such as lithium-rich compounds in the  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  system;<sup>12</sup> and  $\text{LiFePO}_4$  that has an olivine-type structure.<sup>13</sup> Although NCA provides a slightly higher practical capacity (160–180 mAh/g) than  $\text{LiCoO}_2$ , its thermal instability on delithiation due to the presence of the high valence Ni compromises the safety of Li-ion cells. On the other hand, spinel  $\text{LiMn}_2\text{O}_4$  and olivine  $\text{LiFePO}_4$  electrodes are significantly more stable to lithium extraction than the layered Co- and Ni-based electrodes (both structurally and thermally), but they deliver relatively low practical capacities in a lithium cell above 3 V, typically 100–150 mAh/g at moderate current rates.

It became clear by the end of the 1990s that new strategies would have to be developed to design alternative high potential cathode materials (>3 V) with capacities superior to those achievable with standard  $\text{LiCoO}_2$ -,  $\text{LiMn}_2\text{O}_4$ -, and  $\text{LiFePO}_4$ -type electrodes without compromising the structural stability or rate capability of the electrodes or the cycle life of the cells. Recently, researchers at Argonne National Laboratory have developed a family of high-energy manganese-based cathodes by structurally integrating a  $\text{Li}_2\text{MnO}_3$  stabilizing component into an electrochemically active  $\text{LiMO}_2$  (M = Mn, Ni, Co) electrode.<sup>14–16</sup> The relatively high Mn content in these high-energy cathode materials lowers material costs, while the excess lithium boosts specific capacity up to 250 mAh/g between 4.6 and 2.5 V, and therefore, significantly improves the energy density of battery cells to 900 Wh/kg. However, in practical cells, when these high-energy Ni-Mn-Co oxides (NMC) are cycled against graphite, deliverable capacity decreases dramatically with cycle number along with a significant decay of cell discharge voltage.<sup>17</sup> The consequences of the capacity and voltage fading of these materials is the severe loss of the energy density of the cell during long cycling times, which hinders its practical application in electrical vehicles. The underlying mechanisms for the observed energy fading need to be addressed in order to unlock the potential of these compounds as high-energy cathode materials for Li-ion batteries.

Furthermore, since these cathodes operate at a high voltage, there is a need to develop high-voltage electrolytes to enable these new cathodes.<sup>18,19</sup> Several novel organic solvents with greater oxidative stability, such as sulfones,<sup>19</sup> nitriles,<sup>20</sup> and fluorinated solvents,<sup>21</sup> have recently been explored as electrolytes. Unfortunately, these electrolytes may also compromise the anode solid electrolyte interphase-forming reactions required in Li-ion batteries. The development of a novel electrolyte

additive that helps form an interfacial film on the cathode surface is thus important and will likely lead to the development of workable electrolyte systems for high-voltage cathodes.<sup>18</sup>

Since lithium resources are not considered to be abundant, there is the potential for significant cost increase if vehicle electrification expands in the future. As a result, there is growing interest in substituting lithium ions with sodium ions, because sodium is one of the most abundant elements. The article by Kubota et al. in this issue addresses progress in and challenges of sodium ion batteries.

### Anode materials for rechargeable Li-ion batteries

Li batteries with metallic Li anodes offer one of the highest theoretical capacities among conventional battery types, and, in principle, should provide the highest energy density of all Li batteries, primary or secondary, since lithium metal has an extremely high specific capacity (3860 mAh/g) and lower negative redox potential (−3.04 V versus standard hydrogen electrode [SHE]).<sup>22</sup> However, two major technical bottlenecks prevent the realization of a successful rechargeable Li metal battery.<sup>23</sup> One is the growth of lithium dendrites during repeated charge/discharge cycles, which severely compromises the rechargeability of each lithium cell. The rechargeability is affected by the reactions that can take place between the nonaqueous, flammable electrolyte and the cycled lithium anode, leading to the formation of high surface area dendrites. The formation of the lithium dendrites could also lead to serious safety hazards because of the potential for internal short circuits if these dendrites penetrate through the separators and contact the cathode directly. The other bottleneck is low Coulombic efficiency during repeated cycles, although this can be partially compensated for by an excess amount of lithium. For example, in the early development of Li metal batteries, an excess amount of 300% of lithium was typically applied. Overcoming these hurdles presents an enormous challenge to the lithium battery industry.

Recently, researchers demonstrated that the growth of lithium dendrites can be partially prevented through either a physical blocking mechanism (using polyethylene oxide-based block copolymer electrolytes)<sup>24</sup> or a self-healing mechanism (using electrolyte additives).<sup>25</sup> However, these mechanisms are only effective under very limited conditions (i.e., at high temperatures or under low current densities). Therefore, more work is needed to explore a more reliable solution to prevent dendrite growth in order to push the use of lithium anodes for broader applications. Despite these obstacles, significant efforts are under way to capitalize on and exploit the advantages of metallic lithium systems, such as Li-S and Li-air batteries (see the Nazar et al. and Kwabi et al. articles, respectively, in this issue), with a big assumption that these obstacles can be overcome eventually.

The technical hurdles of lithium metal as the anode material have led to the use of carbon-based materials as the most widely used negative electrodes in current rechargeable Li-ion

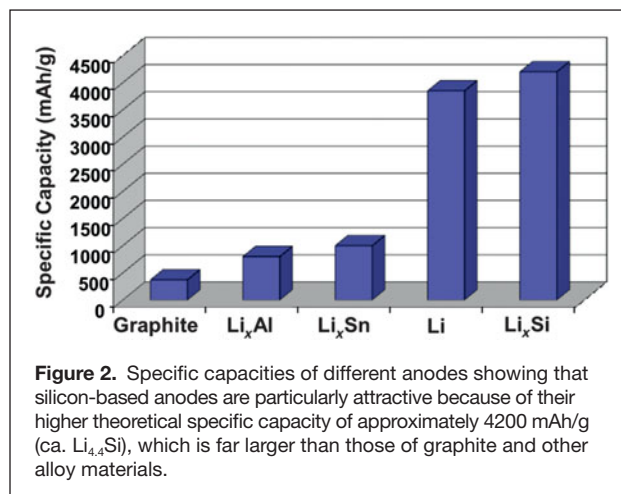
batteries, typically carbon-based materials with the limited specific capacity of graphite (372 mAh/g). In order to overcome the capacity limits of current technology, materials such as Sn, Sb, Si, and Ge,<sup>8,26–28</sup> which form alloys with lithium, have been explored as potentially more attractive anode candidates since they can incorporate larger amounts of lithium (**Figure 2**, Sn and Si are shown because only they have been intensively investigated thus far). Among these, silicon-based anodes are particularly attractive because of their higher theoretical specific capacity of approximately 4200 mAh/g (ca.  $\text{Li}_{4.4}\text{Si}$ ), which is far larger than that of graphite and oxide materials.<sup>27</sup> However, the application of bulk silicon anodes faces one major problem: during the reaction for formation of the silicon-lithium alloy (corresponding to the insertion of lithium in the negative electrode during the charging process), volume expansion from the delithiated phase to the lithiated phase may reach 380%. This high expansion, followed by contraction of the same amplitude (corresponding to the extraction of lithium from the negative electrode during the discharging process), rapidly leads to irreversible mechanical damage to the electrode and eventually to a loss of contact between the negative electrode and the underlying current collector, which causes rapid capacity fade during cycling. Furthermore, silicon usually possesses low electrical conductivity, which has the effect of kinetically limiting the use of the battery. A significant effort is currently under way to enable this system by designing conductive binders that can minimize particle isolation or by incorporating Si in graphene sheets to maintain good conductivity at the electrode level during cycling.<sup>26,29</sup>

### Beyond Li-ion systems

The inherent energy densities of current Li-ion technology are not sufficient for the long-term needs of future applications such as extended-range electrical vehicles. Going beyond Li-ion requires the exploration of new electrochemistries and materials, offering a great opportunity to reach the ultimate goal, although this represents a formidable challenge. In this section, we provide a brief overview of three such systems, rechargeable Li-S, Li-air, and Mg batteries, and we address some of the key challenges for each of these individual systems.

### Li-S batteries

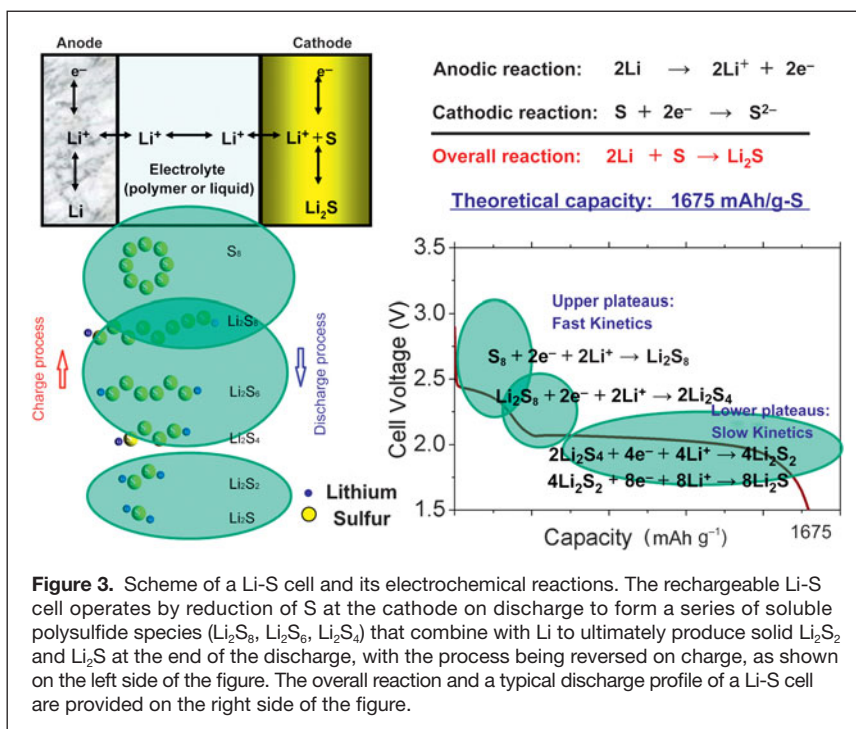
The rechargeable Li-S cell operates by reduction of S at the cathode upon discharge to form a series of soluble polysulfide species ( $\text{Li}_2\text{S}_8$ ,  $\text{Li}_2\text{S}_6$ ,  $\text{Li}_2\text{S}_4$ ) that combine with Li to ultimately produce solid  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  at the end of the discharge, as illustrated in **Figure 3**. On charging,  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  is converted back to S via similar soluble polysulfide intermediates presented in the discharge process and lithium plates to



**Figure 2.** Specific capacities of different anodes showing that silicon-based anodes are particularly attractive because of their higher theoretical specific capacity of approximately 4200 mAh/g (ca.  $\text{Li}_{4.4}\text{Si}$ ), which is far larger than those of graphite and other alloy materials.

the nominal anode, making the cell reversible. This contrasts with conventional Li-ion cells, where the lithium ions are intercalated in the anode and cathode, and consequently the Li-S system, which allows for a much higher lithium storage density.<sup>30,31</sup>

The Li-S batteries, when based on the overall reaction  $\text{S}_8 + 16 \text{Li} = 8 \text{Li}_2\text{S}$ , operate at an average voltage of 2.15 V with a theoretical specific capacity of 1675 mAh/g-S. This leads to an energy density of 2600 Wh/kg (2800 Wh/L), which is five times higher than that of the conventional Li-ion battery based on intercalation compounds. Sulfur is an abundant material available on a large scale and at low cost as a side product of petroleum and mineral refining, which makes it attractive for low-cost and high-energy rechargeable lithium



**Figure 3.** Scheme of a Li-S cell and its electrochemical reactions. The rechargeable Li-S cell operates by reduction of S at the cathode on discharge to form a series of soluble polysulfide species ( $\text{Li}_2\text{S}_8$ ,  $\text{Li}_2\text{S}_6$ ,  $\text{Li}_2\text{S}_4$ ) that combine with Li to ultimately produce solid  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  at the end of the discharge, with the process being reversed on charge, as shown on the left side of the figure. The overall reaction and a typical discharge profile of a Li-S cell are provided on the right side of the figure.

batteries. Furthermore, the unique features of Li-S chemistry provide inherent chemical overcharge protection, which enhances safety, particularly for high-capacity multi-cell battery packs.<sup>30</sup>

Although sulfur-based electrochemical cells had been reported in 1962, initial drawbacks in terms of the electronically insulating nature of sulfur, the solubility of intermediately formed polysulfides in common liquid organic electrolytes, as well as widely known dendrite formation issues accompanying the use of metallic lithium as a negative electrode could not be overcome for several decades and are, in fact, still not solved satisfactorily. In addition, the formed polysulfides in the electrolyte migrate to the lithium metal anode and are electrochemically reduced, well known as a “shuttle reaction,”<sup>32</sup> which results in low Coulombic efficiency and rapid capacity fade in Li-S batteries.

Recently, interest in Li-S based rechargeable batteries has been steadily increasing thanks to the opportunities to design new nanostructured material architectures,<sup>33–35</sup> which could overcome issues related to the bulk material’s conductivity. Moreover, the development of new electrolytes, binder materials, and cell design concepts in general has led to significant advances in the field of Li-S based secondary batteries within the last few years.<sup>31</sup> There is no doubt that Li-S batteries will remain attractive over the longer term because of their inherently high-energy content, high power capability, and potential for low cost, although they are still in the development stage (see the Nazar et al. article in this issue).

### Li-air batteries

Li-air batteries offer superior theoretical energy density and are considered to be the “holy grail” of lithium batteries (**Table I**). The energy density of Li-air batteries is over an order of magnitude higher than Li-ion batteries. Whereas state-of-the-art Li-ion batteries have achieved 150–200 Wh/kg (of the 900 Wh/kg theoretically possible value) at the cell level, Li-air batteries have the potential to achieve 3620 Wh/kg (when discharged to  $\text{Li}_2\text{O}_2$  at 3.1 V) or 5200 Wh/kg (when discharged to  $\text{Li}_2\text{O}$  at 3.1 V). When the “free” oxygen supplied during discharge and released during charge is not included in

the calculation, Li-air cells offer ~11,000 Wh/kg. This is basically identical to the value for gasoline (octane) at ~13,000 Wh/kg when the oxygen that is supplied externally, combusted within, and exhausted from the engine is neglected. Unlike other battery technologies, Li-air is thus competitive with liquid fuels.

During discharge of the Li-air cell, Li is oxidized to  $\text{Li}^+$  at a metallic Li anode, which conducts through an electrolyte composed of a non-aqueous solvent and a Li salt, and reacts with  $\text{O}_2$  from air on a cathode composed of carbon, a catalyst, and a binder deposited on a carbon paper substrate, as shown in **Figure 4**. The Li-air technology has the potential to significantly reduce the cost well below that of the Li-ion battery due to the higher specific energy densities and the lower cost of the proposed cell components, in particular of the carbon-based cathode materials versus the nickel, manganese, cobalt oxides used in Li-ion battery cathodes.<sup>36–38</sup> A non-aqueous electrolyte is preferred, as it has been shown to have higher theoretical energy densities than aqueous electrolyte designs.<sup>39</sup>

Current Li-air batteries are still in the experimental stages, and the realization of the high theoretical energy densities and practical application of this technology have been limited by the low power output (i.e., low current density), poor cycleability, and low energy efficiency of the cell. These limitations are caused by the materials and system design:

- (1) Unstable electrolytes.<sup>40,41</sup> The current non-aqueous, carbonate electrolytes are volatile, unstable at high potentials, easily oxidized, and reduced at the lithium anode in the presence of crossover oxygen. This seriously limits cycle life.
- (2) Lithium electrode poisoning due to oxygen crossover and reaction with the electrolyte destroys the integrity and functioning of the cell.<sup>42</sup> This also lowers cycle life.
- (3)  $\text{Li}_2\text{O}_2$  and/or  $\text{Li}_2\text{O}$  deposition on the carbon cathode surface or within the pores creates clogging and restricts the oxygen flow.<sup>43,44</sup> This lowers capacity.
- (4) Inefficient cathode structure and catalysis.<sup>45–47</sup> Commonly used carbons and cathode catalysts do not access the full capacity of the oxygen electrode and cause significant charge overpotentials. This lowers the power capability.

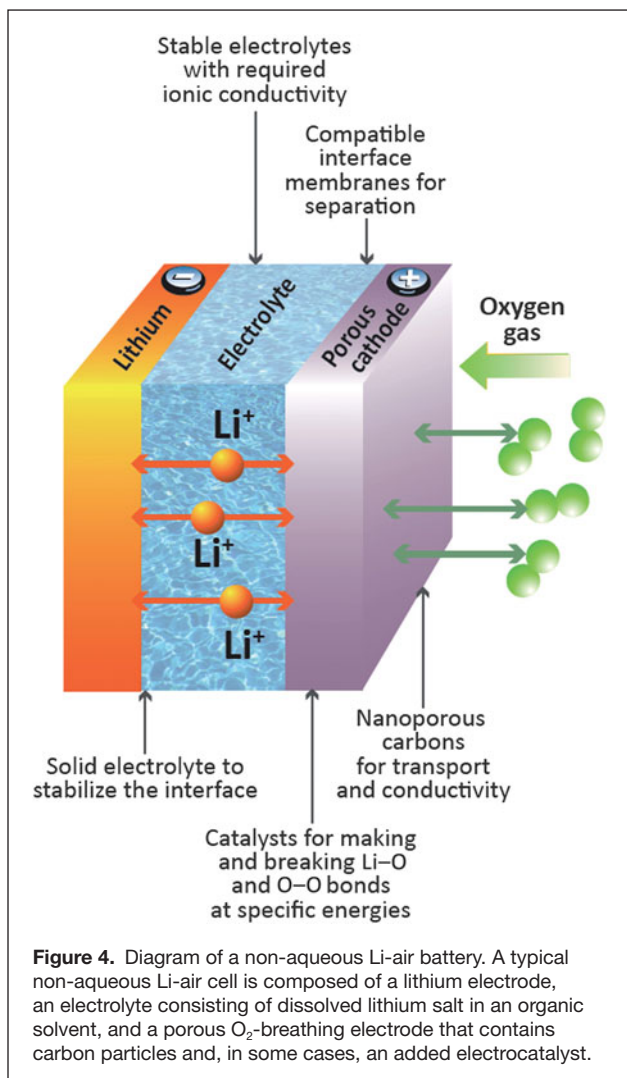
It has recently become apparent that the electrolyte plays a key role in the Li-air cell performance.<sup>48–50</sup> The oxygen anion

radical  $\text{O}_2^-$  intermediate or other reduction species, which may form during the discharge process, can be highly reactive and may cause the electrochemical response to be dominated by electrolyte decomposition rather than the expected lithium peroxide formation. Developing a stable electrolyte<sup>51</sup> as well as the materials and their microstructures in the  $\text{O}_2$ -breathing cathode<sup>52–58</sup> will certainly

**Table I. Relative specific energies of Li/ $\text{O}_2$ , Li/S, Li-ion, and gasoline systems.**

System	Reaction	OCV (V)	Theoretical Specific Energy (Wh/kg)
Li/ $\text{O}_2$	$2\text{Li} + \text{O}_2 = \text{Li}_2\text{O}_2$	3.1	3623 (including O)
	$4\text{Li} + \text{O}_2 = 2\text{Li}_2\text{O}$	2.9	5204 (including O)
	$4\text{Li} + \text{O}_2 = 2\text{Li}_2\text{O}$	2.9	11,202 (excluding O)
Li/S	$16\text{Li} + \text{S}_8 = 8\text{Li}_2\text{S}$	2.0	2600
Li-ion (e.g., $\text{C}_6/\text{LiMO}_2$ [M = Mn, Ni, Co])	$\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{MO}_2 = \text{C}_6 + \text{LiMO}_2$	3.6	~900
Gasoline (octane)	$\text{C}_8\text{H}_{18} + 12.5\text{O}_2 = 8\text{CO}_2 + 9\text{H}_2\text{O}$	–	~13,000 (excluding O)

Note: OCV, open-circuit voltage



advance Li-air technology close to application. For further insights into Li-air batteries, see the article by Kwabi et al. in this issue.

### Rechargeable magnesium batteries

Mg-based batteries are, in principle, a very attractive alternative to other batteries, including Li batteries. Mg is much less expensive than Li because Mg is abundant in the Earth's crust. Mg and its compounds are usually less toxic and safer than Li-based ones because they are stable when exposed to the atmosphere. Mg is also lightweight which, in theory, could enhance the volumetric energy density of the cell (see the article by Shterenberg et al. in this issue).

Rechargeable Mg batteries have been regarded as a highly promising technology for energy storage and conversion since the first working prototype was ready for demonstration about a decade ago, which could compete with lead-acid or Ni-Cd batteries in terms of energy density and self-discharge rate.<sup>4</sup> Since Mg provides two electrons per atom with electrochemical characteristics similar to Li, Mg

batteries offer a theoretical specific capacity of 2205 mAh/g. Proper design and architecture should lead to Mg-based batteries with energy densities of 400–1100 Wh/kg for an open-circuit voltage in the range of 0.8–2.1 V, which would make it an attractive candidate for electrical grid energy and stationary back-up energy storage.

Two major breakthroughs enabled the first demonstration of rechargeable Mg batteries: the development of a non-Grignard Mg complex electrolyte with reasonably wide electrochemical windows, allowing Mg electrodes to be fully reversible,<sup>59</sup> and the discovery of Chevrel-phase-based Mg cathodes with high rate performance.<sup>60</sup> However, the energy density and rate capability of these Mg battery prototypes were still not attractive enough to commercialize them. Moreover, Mg batteries suffer from several serious limitations, including incompatibility between the anode and electrolyte, instability and narrow electrochemical window of the electrolytes, and a slow diffusion rate of  $Mg^{2+}$  cations in the solid-state phase.<sup>4</sup> For further information about rechargeable Mg batteries, see the article by Shterenberg et al. in this issue.

### In this issue

Croy et al. present a detailed description of next-generation Li-ion batteries by including near-term advancements in high-energy lithium-metal-oxide cathode materials, high-energy alloy and oxide anode materials, and high-voltage fluorine-based electrolytes. These high energy and high voltage chemistries are expected to be used in future all-electric vehicles. Furthermore, there is increasing interest worldwide in developing low cost and sustainable systems for grid energy storage that does not use lithium. Rechargeable Na-ion batteries, due to the almost infinite supply of Na, are the most appealing as an immediate alternative to lithium batteries. In this issue, Kubota et al. and Yamada describe the progress, challenges, and future directions for rechargeable Na-ion batteries, with particular focus on the layered oxide (Kubota et al.) and iron-based (Yamada) cathode materials.

Lithium metal could be an ideal anode for next-generation high-energy rechargeable batteries, including Li-sulfur and Li-air batteries. However, two major technical bottlenecks prevent the realization of a successful rechargeable Li metal battery (i.e., the growth of dendrites and low Coulombic efficiency). Vaughey et al. describe several approaches to stabilize the surface of lithium metal and minimize the dendritic growth. This article will also offer a detailed description of the technologies beyond Li-ion, such as Li-sulfur and Li-air batteries, as reviewed by Nazar et al. and Kwabi et al., respectively. Enabling technologies beyond lithium ion will lead to significant cost reduction and an increase in the electrical driving range, leading to an expansion in the electrification of vehicles. The final article of this issue by Shterenberg et al. details the challenge of developing rechargeable magnesium batteries.

### Concluding remarks

This overview article presents a brief glimpse into rechargeable Li/Mg batteries as energy storage and conversion devices for

electrical vehicle and grid applications. These battery systems include rechargeable Li-ion batteries with specific emphasis on high-energy cathode based Li-ion cells, rechargeable Li-S, Li-air, and Mg batteries, which possess the electrochemistries that go beyond the conventional intercalated Li-ion systems. Future requirements for batteries demand innovative concepts for charge storage at the interface of the electrode and electrolyte. These concepts will be realized only by gaining a fundamental understanding of the chemical and physical processes that occur at this complex interface.

Our hope is that the concepts and results presented in this issue of *MRS Bulletin* will prompt new researchers to join this field and help broaden the scope and impact of rechargeable Li/Mg batteries. While valuable progress has been achieved over the past decades, we believe that the most significant advancements and impacts still await discovery and understanding, which could help realize a true transition to an electrified transportation system in the near future.

### Acknowledgments

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