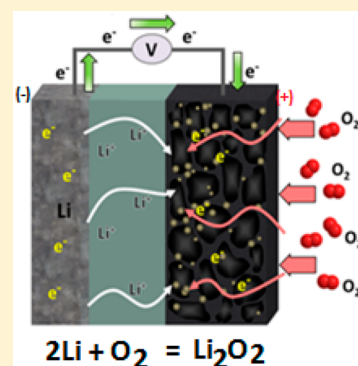


Prospects and Limits of Energy Storage in Batteries

K. M. Abraham*

Department of Chemistry and Chemical Biology, Northeastern University Center for Renewable Energy Technology, Northeastern University, Boston, Massachusetts 02115, United States

ABSTRACT: Energy densities of Li ion batteries, limited by the capacities of cathode materials, must increase by a factor of 2 or more to give all-electric automobiles a 300 mile driving range on a single charge. Battery chemical couples with very low equivalent weights have to be sought to produce such batteries. Advanced Li ion batteries may not be able to meet this challenge in the near term. The state-of-the-art of Li ion batteries is discussed, and the challenges of developing ultrahigh energy density rechargeable batteries are identified. Examples of ultrahigh energy density battery chemical couples include Li/O₂, Li/S, Li/metal halide, and Li/metal oxide systems. Future efforts are also expected to involve all-solid-state batteries with performance similar to their liquid electrolyte counterparts, biodegradable batteries to address environmental challenges, and low-cost long cycle-life batteries for large-scale energy storage. Ultimately, energy densities of electrochemical energy storage systems are limited by chemistry constraints.



A recent report in *Popular Mechanics*¹ identified smartphones as the number one device that changed the world. What was not mentioned in that article was the role played by lithium ion (Li ion) batteries in placing smartphones in this enviable position of world-changing devices. The portable electronic devices indispensable for everyday life such as smartphones, music players, digital cameras, laptop computers, and tablets would not have been possible without Li ion batteries. These high energy density rechargeable batteries are also becoming the power sources of choice for electric vehicles and large-scale storage systems for alternative energy sources such as wind and solar power. The unparalleled superiority of Li ion batteries over other commercial rechargeable batteries is illustrated by the specific energies (Wh/kg) and energy densities (W h/L) of the major batteries, lead–acid (Pb–acid), nickel–cadmium (Ni–Cd), nickel–metal hydride (Ni–MH), nickel–zinc (Ni–Zn), silver–zinc (Ag–Zn), and Li ion, compared in Table 1.

An understanding of the state-of-the-art of Li ion batteries, their future trend, and the prospects and limits of electrochemical energy storage in general are extremely important to technologists involved in the design and development of new consumer products and scientists and engineers engaged in the invention and development of advanced materials for future

high energy density batteries. This account is not a comprehensive review of rechargeable batteries; rather, it is a narrative of the author's perspective on the prospects for electrochemical energy storage, its limitations, and the challenges for developing advanced batteries. I have drawn from my published and unpublished work to write this account, and wherever necessary, I have cited the work of others to support the message being advanced.

There is an ever increasing need for rechargeable batteries with significantly higher energy and power densities in order to meet the growing demands for portable consumer devices with advanced functionalities and long-range electric automobiles.

State-of-the-Art Li Ion Batteries. A typical Li ion battery is composed of a graphite negative electrode (anode) and a transition-metal oxide positive electrode (cathode), which are electronically isolated from each other by means of a porous polyethylene or a polypropylene thin film separator and filled with a Li ion-conducting organic liquid electrolyte, as depicted in Figure 1. The typical electrolyte is a solution of LiPF₆ dissolved in an organic carbonate solvent mixture, usually ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC).²

Table 1. Specific Energy and Energy Densities of Commercial Rechargeable Batteries

rechargeable battery	specific energy, W h/kg	energy density, W h/L
Pb–acid	30	80
Ni–Cd	40	90
Ni–MH	55	165
Ni–Zn	70	145
Ag–Zn	75	200
Li ion	265	690

Received: December 12, 2014

Accepted: February 11, 2015

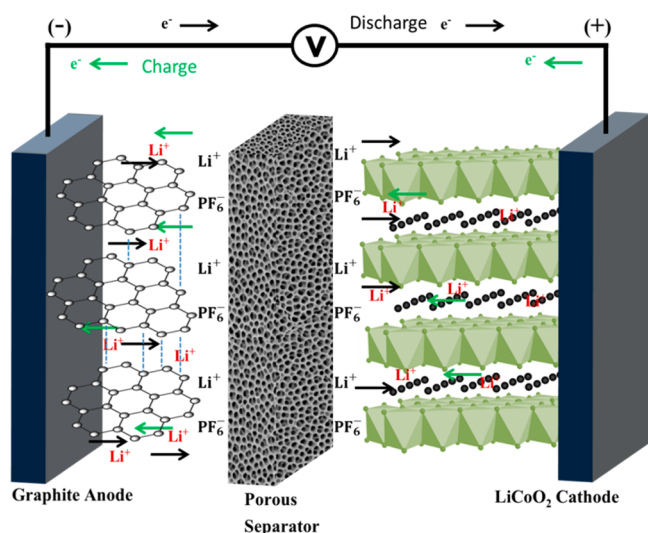
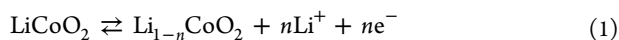


Figure 1. Schematic representation of a Li ion cell. Fabricated in the discharged state, the cell is activated by charging, during which the cathode is oxidized (see eq 1 for the LiCoO₂ cathode) to produce Li⁺ and electrons (e⁻). The Li⁺ travels through the electrolyte (composed of LiPF₆ in organic solvent) and is inserted into the anode (see eq 2 for the graphite anode) along with the electrons arriving at it through the external circuit. The opposite processes occur during discharge.

The reversible electrode reactions during charge and discharge of a Li ion battery involve the intercalation (insertion) and deintercalation (extraction) of Li⁺ into and from the crystal lattice sites of the anode and cathode active materials, with charge-compensating electrons occupying appropriate electronic bands in the respective materials, as depicted in eqs 1 and 2 for the graphite (C₆)/LiCoO₂ battery.² The value of *n* in these reactions is about 0.6.

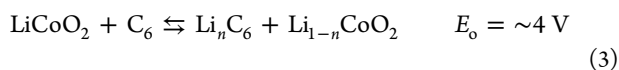
Cathode:



Anode:



Cell reaction:



The standard potential E_0 of the C₆/LiCoO₂ cell is related to the standard free energy of formation (ΔG_0) of the reaction in eq 3, according to eq 4.

$$\Delta G_0 = -nFE_0 \quad (4)$$

where ΔG_0 is the standard free energy of formation of the reaction in eq 3, F is the Faraday constant, and n is the number of electrons involved in the reactions. The electrode materials undergo only small crystal structure changes from the forward and backward reactions in eqs 1 and 2 with the result that the Li ion battery yields a large number of discharge and charge cycles over a wide temperature range. If the Li insertion reaction produces large crystal structure changes in the electrode materials, irreversibility and poor cycle life can be expected from Li ion batteries utilizing them.

The specific energy of a Li ion battery is expressed in Watt-hours per kilogram (W h/kg) according to eq 5

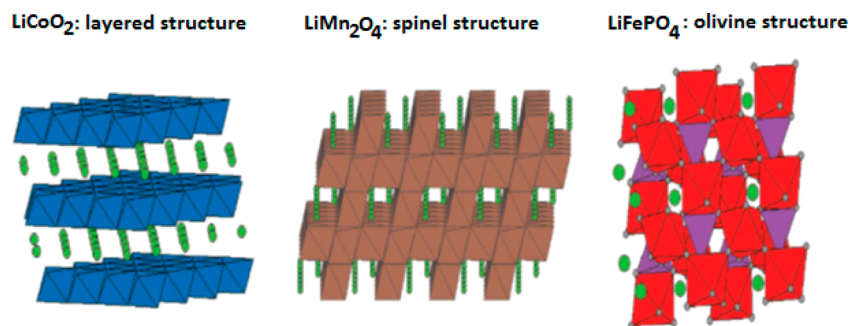
$$\begin{aligned} \text{Specific Energy (W h/kg)} \\ = \frac{\text{Cell Voltage (V)} \times 1000 \text{ (g)} \times 26.8 \text{ A h}}{(\text{kg}) \times \text{equiv wt (g)}} \end{aligned} \quad (5)$$

where V is the cell voltage and 26.8 A h is the Faraday constant, or the theoretical capacity of the electrochemical couple in which the cell reaction involves one equivalent weight (equiv wt) of the electrode reactants. The equivalent weight of an electrochemical couple is obtained by dividing the weight of the electrode reactants (in grams) by the number of electrons transferred in the reaction. The energy density (W h/L) of a Li ion battery is obtained from a similar relationship using the equivalent volumes of the electrode reactants.

The three major classes of cathode materials utilized in commercial Li ion batteries are the layered lithiated transition-metal oxides, exemplified by LiCoO₂ (LCO) and its congeners, LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ (NMC) and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA), lithiated transition-metal spinel oxides, typified by LiMn₂O₄ and LiMn_{1.5}Ni_{0.5}O₂, and lithiated transition-metal phosphates represented by LiFePO₄. The crystal structures of these three prominent classes of cathode materials used to construct commercial Li ion batteries are depicted in Scheme 1. The graphite anode material also has a layered crystal structure.

The graphite anode has a theoretical specific capacity of 370 mAh/gram, involving the transfer of one electron (or one equivalent of Li) per mole of C₆. All of this capacity can be accessed practically in a Li ion cell conforming to the graphite electrode half-cell reaction shown in eq 2. The types of graphite used as anode active materials in Li ion batteries include natural

Scheme 1. Crystal Structures of Cathode Materials for Li Ion Batteries^a



^aFrom Thackeray, M. Li Ion Batteries: An Unexpected Conductor. *Nat. Mater.* 2002, 1, 81; reprinted with permission of the publisher.

graphite, synthetic graphite, *meso*-carbon microbead (MCMB) graphite, potato graphite, and graphite whose surface is modified with poorly crystalline carbon.^{2–5} The graphite anode acquires stability in the Li ion battery by forming an insoluble surface film, termed a solid electrolyte interphase (SEI), from electrochemical reaction of the electrolyte. The SEI is impervious to electrons and protects the lithiated graphite electrode from extensive reactions with the electrolyte while allowing the transport of Li⁺, as in a solid electrolyte, to accomplish the electrode reactions.

The voltage versus Li intercalation capacity obtained in a “lithium half-cell” presented in Figure 2 illustrates the SEI

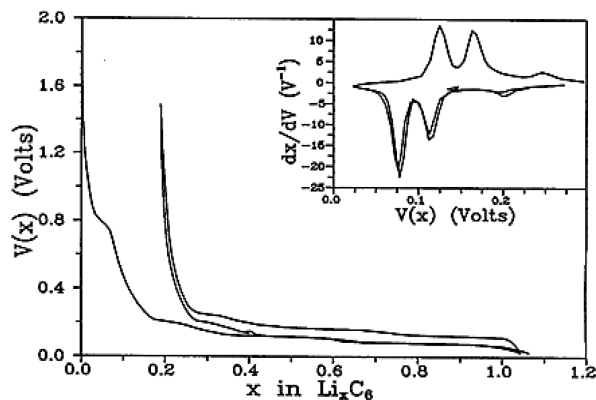
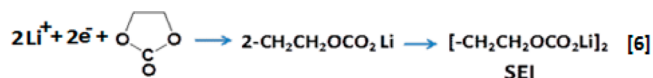


Figure 2. Li intercalation (charge) and deintercalation (discharge) capacities of graphite in a Li half-cell utilizing an organic carbonate-based electrolyte. One mole of Li per mole of C₆ is equivalent to a 370 mA h/g capacity. The inset shows the derivative curves of the charge and discharge processes (from ref 3; reprinted with permission of Elsevier).

formation process in a graphite electrode undergoing Li intercalation and deintercalation. The irreversible capacity appearing in the voltage region between 1.2 and 0.25 V in the first discharge (Li intercalation) of the Li/C₆ cell in Figure 2 is used for the SEI formation. The SEI is believed to be a lithiated organic carbonate polymer formed from electrochemical reduction of EC, as shown in eq 6.



The specific energy and energy density of commercial Li ion batteries are limited by the reversible intercalation capacities of the cathode materials. The theoretical capacity of lithiated layered transition-metal oxide of the formula LiMO₂, where M is Co or Ni, is about 273 mA h/g, corresponding to the

extraction of one mole of Li (or one electron) per mole of transition metal. Only fractions of this capacity can be reversibly accessed in Li ion cells. This is because the overcharged Li_{1–n}CoO₂ and Li_{1–n}NiO₂ become unstable as the tetravalent oxides of Ni and Co do not exist and they decompose to lower-valent metal oxide phases. The properties of the most prominent commercial Li ion batteries are summarized in Table 2.

Energy and Power of Li Ion Batteries. The energy (in Wh) of a battery is given by the product of its capacity in Ah and load voltage, *V*. The specific energy (Wh/kg) is the energy per unit mass (kg), and the energy density (Wh/L) is the energy per unit volume (L) of the battery.

The power output (*W*) of a battery is given by eq 7⁶

$$\text{Power (W)} = V \cdot I \quad (7)$$

where *V* is the load voltage and *I* is the current drawn from the battery.

From Ohm's law, $V = I \cdot R$. Therefore

$$W = \frac{V_{\text{load}}^2}{R} \quad (8)$$

In eq 8, $V_{\text{load}} = E - \Delta E_p$, and *R* is the sum of the battery's resistances, which include the internal resistance *R_i* and the load resistance *R_{load}*; *E* is the open-circuit voltage of the cell and ΔE_p is the total voltage loss, that is, polarization in the cell from (i) the electrical resistances of the electrodes, *R_e*, (ii) the ionic resistance of the bulk electrolyte, *R_{el}*, (iii) the effective ionic resistance in the porous electrode, *R_{ion}*, (iv) the resistance to charge transfer during Li ion intercalation and deintercalation, *R_{ct}*, (v) electrical contact resistances in the external circuit that are normally very small, *R_{con}*, and (vi) finally, the load resistance, *R_{load}*. A detailed discussion of these various factors is given in our recent paper.⁶

Nano versus Micron Dilemma for Selecting Electrode Materials. The choice of nano or micron size electrode material particles to fabricate porous electrodes for Li ion batteries will depend on the Li⁺ diffusion coefficient, *D_{Li+}*, in the Li intercalating solid anode and cathode materials and the power output required from the battery. Equation 9 relates the diffusion coefficient of Li⁺ and its diffusion length in the intercalation host material particle

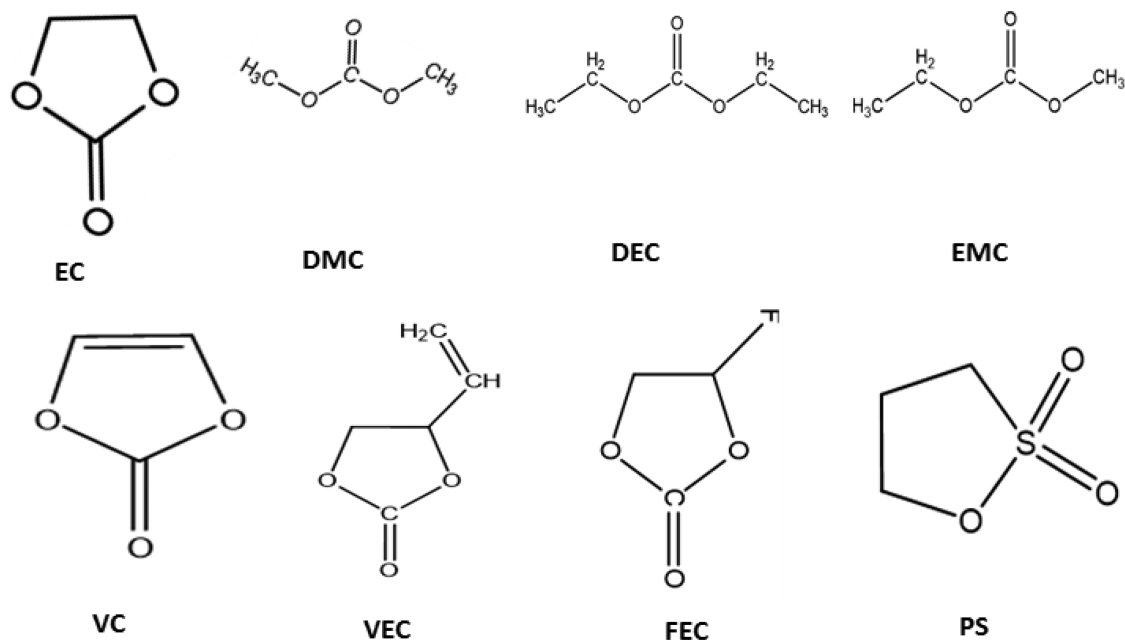
$$D_{\text{Li}^+} = \frac{l^2}{t} \quad (9)$$

where *l* is the radius (half of the diameter or size) of the electrode particle (in cm) and *t* is the time (in seconds) for Li⁺ diffusion in the solid particle.^{6,7}

Table 2. Theoretical and Practical Specific Energy and Energy Densities of Commercial Li Ion Batteries

Li ion battery	voltage, V	theoretical specific energy, Wh/kg	theoretical energy density, Wh/L	18650-size Li ion cell capacity, Ah	specific energy of 18650-size Li ion cell, Wh/kg	energy density of 18650-size Li ion cell, Wh/L
graphite(C)/ LiCoO ₂ (0.6 electron reaction)	3.7	420	1597	2.4	206	530
C/LiNi _{0.33} Mn _{0.33} Co _{0.33} O ₂ (0.7 electron reaction)	3.6	450	1561	2.4	210	530
C/LiN _{0.8} Co _{0.15} Al _{0.05} O ₂ (0.75 electron reaction)	3.6	470	1597	3.2	265	690
C/LiFePO ₄ (1.0 electron reaction)	3.4	370	1126	1.6	126	325
C/LMn ₂ O ₄ (0.8 electron reaction)	3.8	330	1146	1.5	132	340

Scheme 2. Structural Formulas of Solvents and Additives Used in Li Ion Battery Electrolytes



It can be shown that when D_{Li^+} is 10^{-10} cm^2/s , the electrode particle will have to be about $1.5 \mu\text{m}$ (1.5×10^{-4} cm) in diameter in order to achieve its full electrochemical utilization in 60 s, the time corresponding to the 60C discharge rate in a Li ion cell. (A C-rate corresponds to full discharge of the battery in 1 h and the 60C rate involves discharge in 1/60 of an hour, or 1 min). This implies that with these $1.5 \mu\text{m}$ particles, solid-state diffusion of Li^+ will not be the limiting step for up to about 60C rates of discharge of the battery. In other words, when materials with such a high D_{Li^+} are used in Li ion batteries, only micron size particles are needed for applications requiring 60C or lower rates.

If the solid-state diffusion coefficient of Li^+ is very low as in LiFePO_4 , with a D_{Li^+} of about 10^{-14} cm^2/s ,⁸ then the electrode particles must be about 15 nm (15×10^{-7} cm) or smaller to achieve full discharge of the electrode in 60 s or shorter time. Indeed, high-power commercial graphite/ LiFePO_4 Li ion batteries, capable of 10C–30C discharge rates for applications in power tools and hybrid electric vehicles, use micron size (4–6 μm) graphite particles (D_{Li^+} graphite is about 10^{-10} cm^2/s) and nanometer size (25–100 nm) LiFePO_4 particles, underscoring the validity of the discussion.

It should be noted that for materials such as LiFePO_4 exhibiting a two-phase ($\text{LiFePO}_4/\text{FePO}_4$) discharge reaction, an alternate explanation for improved discharge rates in nanomaterials is the suppression of phase separation between the lithiated and delithiated phases, as advocated by Bazant.⁹ It can be concluded that when the solid-state Li^+ diffusion coefficient in the electrode materials is about 10^{-10} cm^2/s or higher, micron size electrode materials are adequate to achieve 10C–50C discharge rates from the Li ion battery, provided that the internal resistance of the cell is optimized to achieve the high current drains per eq 8. When the Li^+ diffusion coefficient is low, as in LiFePO_4 , nanometer size electrode particles are used to fabricate high-power batteries exhibiting these same magnitudes of charge and discharge rates. It is important to be mindful of the deleterious side effects of nanomaterials when they are being considered for use in practical batteries.

Nanophase materials have higher surface areas than their micron counterparts, which bring about the possibility of increased reactivity of the nanomaterials with electrolytes, leading to internal impedance rise, decrease in rate capability, and accelerated capacity fade of batteries built with them. It should be noted that the reactivity of nanomaterials with electrolytes becomes an issue only if the electrolyte's stability window is lower than the operating voltage of the electrode material. If this condition is not met, the electrode materials will not react with the electrolyte. This is illustrated by the electrochemical performance of the graphite/ LiFePO_4 cell in which the nanophase LiFePO_4 operates below the decomposition voltage of organic carbonate-based electrolytes and the cell has exceptional stability, as demonstrated by thousands of charge/discharge cycles. On the other hand, 4 V nanophase electrode materials such as LiCoO_2 and LiMn_2O_4 exhibit high reactivity and poor stability in contact with Li ion battery electrolytes.

Li Ion Battery Electrolytes. A typical Li ion battery electrolyte is composed of 1–1.2 M LiPF_6 dissolved in a 1:1:1 by volume mixture of EC, DMC, and DEC. The Li^+ diffusion coefficient of liquid electrolytes, which is related to their ionic conductivity, is about 10^{-6} cm^2/s , 3–6 orders of magnitude higher than the Li^+ diffusion rates in solid-state intercalation electrodes. Electrolytes for Li ion batteries must have several desirable properties, including a high ionic conductivity of about 10^{-2} S/cm, a wide voltage window of electrochemical stability, and the ability to function over the temperature range from at least -20 to 60 °C. In addition, liquid electrolytes must form stable Li ion-conducting SEI on the electrodes, especially the anode.

Electrolyte additives, such as vinylene carbonate (VC), 1,3-propane sultone (PS), fluoroethylene carbonate (FEC), and vinyl ethylene carbonate (VEC), have been identified to optimize the properties of the SEI on the anode and cathode.^{2,4} The structural formulas of typical organic solvents and additives used in Li ion batteries are presented in Scheme 2. Electrolyte additives are also used for deactivating the PF_5 produced by the dissociation of LiPF_6 ,¹⁰ scavenging impurities,¹¹ overcharge

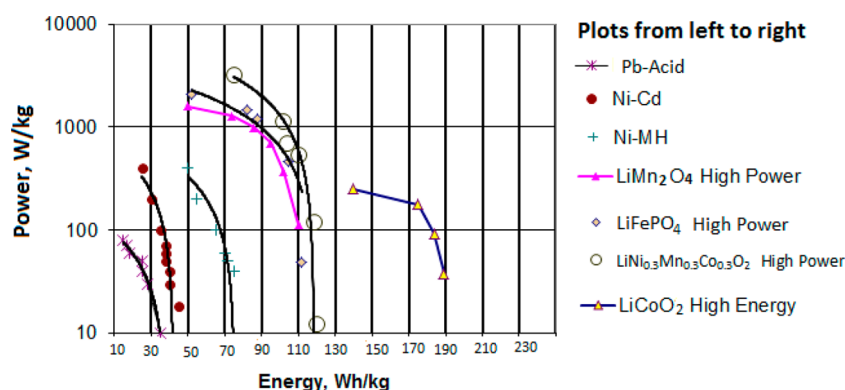


Figure 3. Ragone plots relating the power density and energy density of rechargeable batteries. The plots were drawn using data for commercial Pb–acid, Ni–Cd, Ni–MH, high-power Li ion 18650 cells (using LiMn_2O_4 , LiFePO_4 , and $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ cathodes and graphite anodes), and a high-energy Li ion cell with a LiCoO_2 cathode and graphite anode.

protection of Li cells,¹² as flame retardants,¹³ and for cell shutdown upon the initiation of a thermal runaway reaction.¹⁴ Recent reviews of additives for Li ion batteries by Lucht et al.¹⁵ and Wilken et al.¹⁶ are useful to those interested in entering the field.

Steady-State versus Pulse Discharge of Li Ion Cells. Li ion batteries are used for a range of applications including pulse power discharges involving very short discharge times of milliseconds to seconds and steady-state discharges encompassing many minutes to hours. In a short pulse discharge, the power output is primarily controlled by the internal resistance of the cell according to eqs 7 and 8, and the voltage and current of the cell under this condition are governed by Ohm's law, $E = I \cdot R$. For long discharge times of minutes to hours, the steady-state power output of the cell is determined by the limiting current, I_l , according to eq 10¹⁷

$$I_l = \frac{2nFCD}{(1 - t^+)}l \quad (10)$$

where F is the Faraday constant, C is the concentration of the electrolyte, n is the number of equivalents of electrons transferred, D is the diffusion coefficient of Li^+ in the electrolyte, l is the interelectrode distance including the thickness of the porous electrode, and t^+ is the transport number of Li^+ in solution, which for organic electrolytes is about 0.3.¹⁷ As mentioned earlier, once the particle size of the intercalation electrode material is chosen for a desired rate based on its D_{Li^+} , according to eq 9, then ion transport in the electrolyte phase of the relatively thick porous electrode becomes the rate-limiting process. Thus, I_l will vary depending on the thickness of the electrode, the electrolyte concentration, and the transport number of Li^+ . In a Li ion cell, the geometric area of the electrode, where the electrochemical reaction occurs, is decreased by the porosity of the porous separator that electronically isolates the two electrodes, as depicted in Figure 1. When the porosity (P) and tortuosity (T) of the separator are introduced into eq 10 to account for the effective area of the electrode for electrochemical reaction, the limiting current from the cell is given by eq 11.^{17,18} However, note that the separator does not change the overall surface area of the electrodes for electrochemical reactions.

$$I_l = \frac{2nFCDP}{T(1 - t^+)}l \quad (11)$$

The selection of separators with appropriate thickness and porosity is very important, especially when designing high-power Li ion batteries.^{17,18} A general method of comparing the energy and power of different battery systems is by means of the Ragone plot,¹⁹ which depicts energy density versus power density, as shown in Figure 3. These data demonstrate the superior energy and power capabilities of Li ion batteries compared to conventional aqueous batteries such as Pb–acid, Ni–Cd, and Ni–MH.

Cycle Life of Li Ion Batteries. The generally agreed upon definition of the cycle life of Li ion batteries is the number of times they can be fully discharged and charged before the capacity decreases to 80% of the initial value. Battery cycle life depends on many factors, including the discharge and charge rates, the voltage limits to which the battery is charged and discharged, the electrolyte and the impurities that it contains, the electrode materials with which they are built, and the operating temperature. The capacity versus cycle number plot for a 2 A h nominal capacity high-power Li ion cell, composed of a MCMB graphite anode, NMC cathode, and electrolyte of 1.2 M LiPF_6 dissolved in a 1:1:1 by volume mixture of EC, DMC, and DEC, is shown in Figure 4,¹⁸ along with several of its high-rate discharges. This 2 A h high power battery cell was cycled at room temperature at the 1C discharge and charge

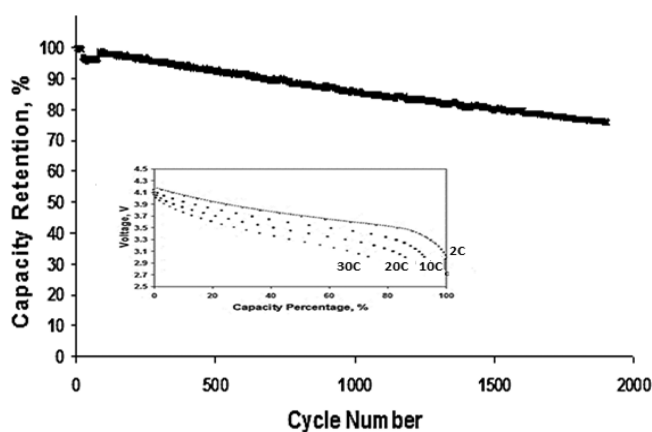


Figure 4. A typical cycle life plot for a 2 A h Li ion battery cell depicting capacity versus cycle number. The cell was built with a graphite anode and NMC cathode and cycled at 1C charge and discharge rates between the voltage limits of 2.9 and 4.2 V (the inset shows discharges at different C-rates (from ref 18)).

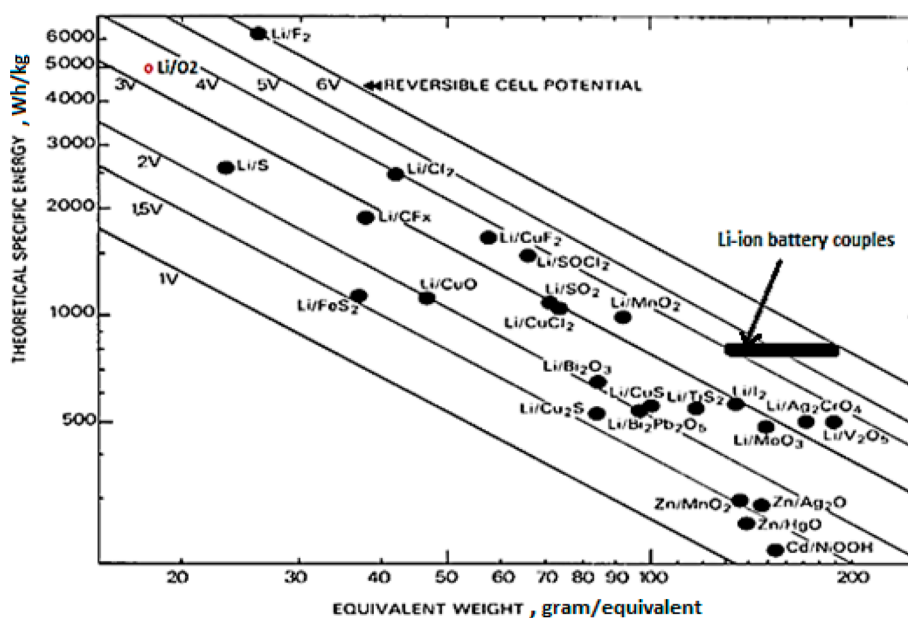


Figure 5. Energy density map depicting theoretical energy densities versus equivalent weights of battery couples for various cell voltages. This is a modified version of Figure 1 from *Lithium Batteries*, Chapter 1, edited by J. P. Gabano, Elsevier 1983. (Adapted with permission of Elsevier).

rates with a discharge voltage limit of 2.9 V and charge voltage limit of 4.2 V.

The capacity versus cycle number of Li ion cells usually follows an exponential decay (fade) function, expressed by eq 12. This equation can be used to predict the cycle life of a cell, knowing the value of x , the initial cell capacity (Q_0), and the capacity at the N th cycle, Q_N .²⁰ A is a constant which determines the rate of capacity fade. The value of x for the cell in Figure 4 is 0.7.

$$Q_N = Q_0 - A \cdot N^x \quad (12)$$

It should be noted that different mathematical models, taking into account input parameters such as temperature, charge and discharge current densities and voltage limits, and the chemical degradation properties of the electrodes and electrolytes, have been developed to characterize the performance and forecast the cycle life of Li ion batteries.^{21,22} Models for predicting the cycle life of Li ion batteries should be carefully developed, with attention paid to understand the clear role of each of these factors.

Energy Content and Safety of Li Ion Batteries. The total heat produced from a Li ion cell in the event of an internal short circuit and the maximum temperature that a cell will experience from this heat can be calculated, given the specific heat of the cell. The specific heat of a typical Li ion cell has been measured experimentally to be 1 J/K/g.²³ A state-of-the-art 18650-size Li ion cell with a 3.2 A h capacity and an average voltage of 3.6 V produce 11.5 W h (41400 J) of energy. The weight of the 18650-size cell is about 46 g. We can calculate from these parameters that the 41400 J of heat will raise the temperature of the 46 g cell by 900 °C. That means that if an 18650-size Li ion cell operating at 20 °C short circuits internally, its temperature under adiabatic conditions can rise to as high as 920 °C (900 + 20 = 920 °C). At such a high heat, the graphite anode will lose its SEI stability, the polymer separator will melt, the cathode will decompose, and the Al current collector will melt and react with the electrolyte and other cell components, generating additional heat. Clearly, the high heat output possible from Li

ion batteries explains the occasional incidents of fire and explosion originating from manufacturing defects of commercial cells. A number of chemical approaches are pursued to improve the safety of Li ion batteries, and they include the use of nonflammable electrolytes, particularly those based on organic fluorides,²⁴ fire-retardant additives such as organophosphorus compounds like triphenyl phosphine,²⁵ and redox shuttle reagents^{12,14} that lock the cell's charge voltage at an appropriate value below the electrochemical decomposition voltages of the electrolyte and the positive electrode. In commercial Li ion battery packs, individual cell voltage cutoff and capacity balancing are accomplished by means of electronic circuitry. Replacing these with chemical redox shuttle reagents would increase the energy density and lower the cost of Li ion batteries.

Prospects and Challenges of Advanced Battery Materials and Systems. There is an ever increasing need for batteries with significantly higher energy and power densities in order to meet the growing demands for new portable consumer devices with advanced functionalities, long-range electric automobiles, aerospace vehicles, improved power tools, electricity storage for utilities, and many other energy-hungry applications. The case for the all-electric family of automobiles with a driving range of 300 miles or more on a single charge illustrates the need for ultrahigh energy density rechargeable batteries with 2–3 times larger energy density than today's best Li ion batteries.²⁶ I have shown that the energy density required for the battery cells to build battery packs capable of giving 300 mile range electric vehicles would be about 580 W h/kg, more than twice that of today's Li ion cells.^{4,26} In order to build such Li ion batteries, future emphasis should be given to developing cathode active materials with significantly higher specific capacities. The challenge is to identify battery couples capable of ultrahigh energy densities and very long cycle life.

Ultrahigh Energy Density Rechargeable Batteries. Rechargeable batteries having significantly higher energy densities than today's Li ion batteries may be identified from battery chemical couples based on anode and cathode active materials having

low equivalent weights, as shown by eq 5. For anode active material, Li is preferred because of its low equivalent weight and the ability to form high-voltage chemical couples. Figure 5 is an energy density map depicting theoretical energy densities versus equivalent weights of battery couples for various cell voltages. It illustrates that coupling the most electropositive element Li with the highly electronegative and light elements from groups VIB and VIIB of the periodic table, or compounds formed with them, provides the best opportunities for building super high energy density batteries. Figure 6 displays the theoretical energy densities of several ultrahigh energy density Li battery couples along with those of some well-known practical batteries and the H_2/O_2 fuel cell.

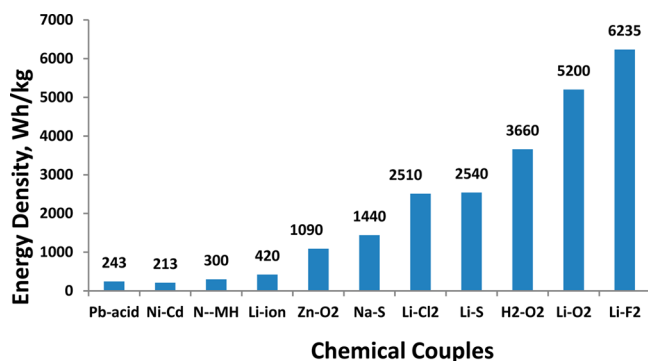


Figure 6. Theoretical specific energies of battery chemical couples. The number above each bar represents the theoretical specific energy of the battery. (See also ref 26.)

The lithium–fluorine (Li/F₂) chemical couple is the highest energy density battery theoretically possible, but it is impractical because of the extremely high chemical reactivity of F₂. Similarly, the Li/Cl₂ couple is a difficult system to implement as a practical battery because of the reactivity and toxicity of Cl₂. This leads to the Li/O₂ couple as the most logical candidate for the ultimate high energy density battery. The Li/S system enjoys a distant second place in the hierarchy of ultrahigh energy density batteries. This author has had a major role in pioneering both of these rechargeable batteries.

The information provided in Figures 5 and 6 also underscores the fact that ultimately there is a limit in the energy density of energy storage systems that can be developed via electrochemical reactions. Certainly, many new rechargeable systems could emerge in the future, but their energy densities would not exceed those projected by the data in Figures 5 and 6. In the following sections, I discuss the challenges of developing high energy density batteries beyond Li ion systems.

Materials Challenges of Li Ion Batteries beyond Today's Systems. The equivalent weights of Li ion batteries range from about 100 g/equiv (for the best case scenario for a chemical couple utilizing a silicon anode capable of reversibly alloying 4 mol of Li per mole of Si and a lithiated metal oxide cathode active material with a specific capacity of 270 mA h/g) to 235 g/equiv (for the graphite/LiCoO₂ battery utilizing 0.6 mol of Li per mole of LiCoO₂ to give a reversible capacity of 140 mA h/g). Clearly, the Li ion battery couples with equivalent weights significantly less than 100 g/equiv must be developed in order to produce ultrahigh energy density batteries having much higher energy density than that possible today.

The evolution in the energy density of Li ion batteries is presented in Figure 7 using the highly engineered 18650

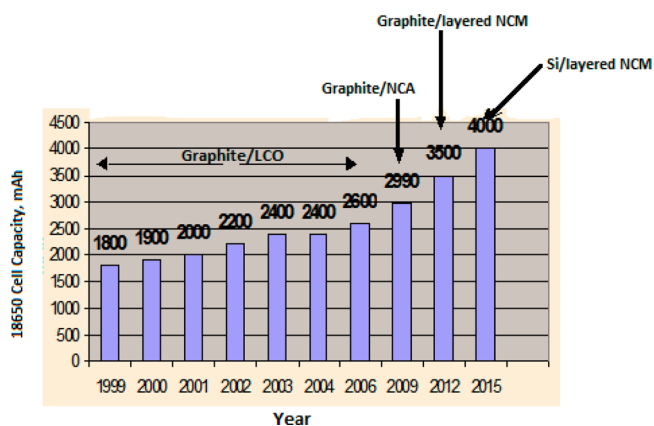


Figure 7. Energy progression of Li ion batteries with 18650 size commercial cells as examples (see also ref 26). The numbers on the bars in the graph are 18650 cell capacities in mA h. (LCO is LiCoO₂, NCA is LiNi_{0.8}Co_{0.15}Al_{0.05}O₂, and NCM is lithium-rich layered nickel manganese cobalt oxide, Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ and structural analogues).

commercial cells as examples. Clearly, the energy densities of state-of-the-art cells or those projected for introduction in the near future fall short of the 580 W h/kg cells required for the 300-mile vehicles. The lithium-rich layered manganese oxides (layered LMO)²⁷ and their structural analogues, for example, Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O₂ (called layered NCM), have shown practical reversible capacities up to 270 mA h/g, albeit at low rates.^{27,28}

The specific energy of the 18650 Li ion cells built with the NCM cathode and graphite anode is 280 W h/kg (3.6 A h at 3.6 V in an 18650 cell), increasing to approximately 320 W h/kg (4 A h 18650 cell) if the graphite negative electrode is replaced with silicon. It should be noted that the development of Li-alloying anode materials such as Si, Sn, and other metals poses development challenges due to the large volume changes accompanying the alloying and dealloying reactions.^{4,5}

It is seen from Figure 5 that the theoretical specific energies of batteries having voltages between and 4 and 5 V and an equivalent weight of 100 would be 1000–1250 W h/kg, with practical batteries yielding specific energies in the range of 500–600 W h/kg, significantly less than that of a Li/O₂ battery. However, available data suggests that the average voltage practically feasible in a metal oxide undergoing two moles of Li intercalation per mole of transition metal (as a compound) would be about 3 V or lower because the second Li is inserted at a much lower voltage than the first. As a result, the theoretical specific energy possible from such batteries is in the 750–1000 W h/kg range. Materials in which a second Li insertion has been attempted include LiVOPO₄,²⁹ A₂FePO₄F (A = Na, Li),³⁰ LiFeSO₄F,³¹ and Li₂FeSiO₄.³²

Many novel Li intercalation electrode materials involving the transfer of multiple Li's (or electrons) per metal for use as cathode and anode active materials for Li ion batteries can be expected in the future, although their energy densities would fall short of the ambitious goals for long-range electric vehicles.

Departing from Li intercalation electrodes to those exhibiting displacement reactions does not change the energy density of the battery as long as the equivalent weight of the battery couples (i.e., the number of electrons transferred per metal) remains the same. Some examples of battery couples exhibiting

the displacement (or popularly known as conversion) electrode reactions are shown in Table 3.

Table 3. Battery Couples with Displacement Electrode Reactions

Li cell and reaction	E_{cell} (V)	equivalent weight (g/equiv)	theoretical specific energy (Wh/kg)
$3\text{Li} + \text{BiF}_3 \rightleftharpoons 3\text{LiF} + \text{Bi}$	3.2	76	1118
$3\text{Li} + \text{FeF}_3 \rightleftharpoons 3\text{LiF} + \text{Fe}$	2.5	45	1488
$2\text{Li} + 2\text{NiO} \rightleftharpoons \text{Li}_2\text{O} + 2\text{Ni}$	1.5	56	1115
$2\text{Li} + \text{S} \rightleftharpoons \text{Li}_2\text{S}$	2.1	23	2540
$4\text{Li} + \text{O}_2 \rightleftharpoons 2\text{Li}_2\text{O}$	2.9	15	5200

Of course, the Li/O₂ and Li/S are the most prominent examples of chemical couples undergoing such electrode reactions. Other examples include the Li/BiF₃, Li/FeF₃, and Li/NiO cells shown in Table 3.^{33–36} Certainly, there is a large number of potential cathode active materials including metal halides, especially fluorides, metal sulfides, metal phosphides, and metal oxides, that can be pursued in the family of conversion electrode materials for Li batteries. The electrode processes in these batteries involve displacement reactions accompanied by bond breaking among their constituent elements with the result that achieving long cycle life in such batteries would be a major challenge. Another apparent drawback of these materials is that the battery requires a metallic Li anode that makes it imperative to overcome the poor cycling efficiency of the Li anode in order for the batteries to achieve long cycle life and acceptable safety characteristics.

Efforts are also being made to develop Na intercalation electrode batteries analogous to the Li intercalation systems operating at room temperature (see ref 3 for recent a review). The major incentives for pursuing Na ion batteries are the abundance of Na and the perceived lower battery cost. Most of the efforts to date have been centered on Na intercalation cathode active materials. Clearly appropriate anode materials have to be developed in order for Na ion batteries to become successful practical systems.

Electrode engineering to improve the rate capability of thick electrodes to gain higher energy density in high-power Li ion batteries remains a challenge. In this respect, the layered electrode architecture based on alternating layers of Li intercalation electrode materials and multiwall carbon nano-

tubes (MWCNTs) to achieve higher discharge rates from high-energy Li ion cells that we have reported⁶ could serve as a model for future efforts.

Rechargeable Li/O₂ Battery. The rechargeable Li/O₂ battery cell with an open-circuit voltage of 2.91 V and a discharge reaction involving the reduction of O₂ by four electrons to form Li₂O has a theoretical specific energy of 5200 W h/kg. As we will see later, the discharge product identified to date in nonaqueous Li/O₂ cells is Li₂O₂, which decreases the theoretical specific energy of this battery to 3505 W h/kg. My colleague and I demonstrated the first nonaqueous rechargeable Li–air battery in 1996.³⁷ More recently, the Li/O₂ battery (popularly known as the Li–air battery because the fully developed battery would access the cathode active material O₂ from the environment) has become the focus of intense worldwide research and development. A schematic representation of a Li–air battery is given in Figure 8. Several review papers summarizing the research and development of the Li–air battery have appeared.^{38–40} The Li–air battery is one of many metal–air batteries that could conceivably be developed (see Table 3 in ref 37), although the systems based on other metals have lower energy densities.

We have shown that the oxygen reduction reaction (ORR) mechanism and the products formed in the nonaqueous Li–air battery can be satisfactorily explained using a general theory, termed the hard–soft acid–base (HSAB) theory.^{41–44} The ORR mechanism and the products formed depend on the acid–base properties of the solvent and the ion-conducting cations present in the nonaqueous electrolyte. The HSAB concept has been formulated from the knowledge that the Li⁺ (and other cations) in nonaqueous electrolytes is a Lewis acid whose acidity is decreased by solvation (complexation) by solvent molecules to form solvates of the formula Li⁺(solvent)_{*n*}, where *n* usually is 4. The solvation decreases the Lewis acidity of Li⁺ in proportion to the basicity of the organic solvent, measured by Gutmann donor number (DN).

The HSAB theory also makes use of the fact that the ORR products (the oxides O₂^{•−}, O₂^{2−}, and O^{2−}) are Lewis bases whose basicity increases as the number of electrons transferred per O₂ is increased from one to four. We have found that in electrolytes based on organic solvents and ionic liquids, the initial O₂ reduction reaction involves a one-electron transfer to O₂ to form the superoxide radical ion, O₂^{•−}. The relative lifetime of this superoxide depends on the Lewis acidity of the cation present in the electrolyte, whether it is a tetraalkyl ammonium, a solvated Li⁺, or an ionic liquid cation. These

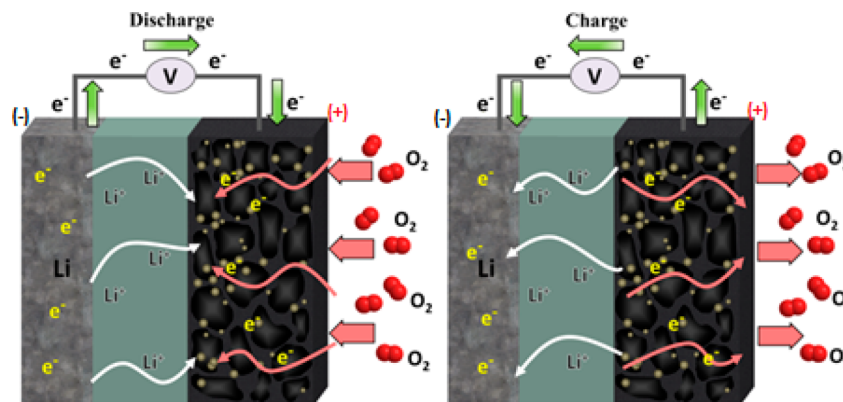
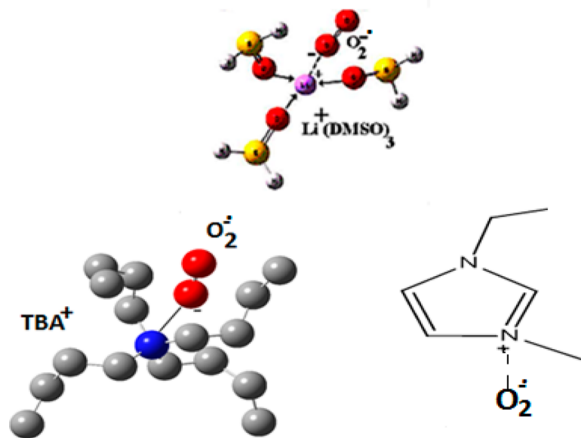


Figure 8. Schematic of a Li–air battery showing its discharge (left) and charge (right).

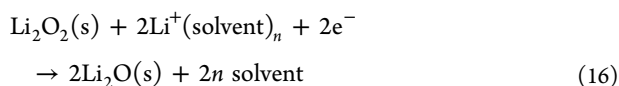
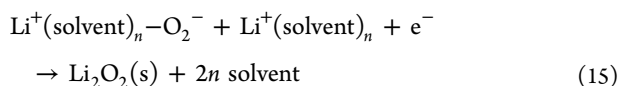
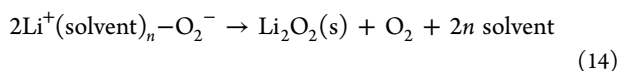
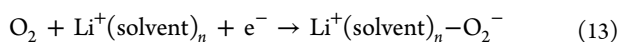
cations stabilize the superoxide to varying lengths of time in the electrolyte by forming ion pairs of the type shown in Scheme 3.

Scheme 3. Schematic Representation of the Ion Pair Formed between the Dimethyl Sulfoxide (DMSO) Solvated Li^+ ($\text{Li}^+(\text{DMSO})_n$), Tetrabutyl Ammonium (TBA^+), and Ethyl Methyl Imidazolium (EMI^+) Cations and $\text{O}_2^{-\bullet}$ ^a



^aFrom ref 41.

The multistep electrochemical reduction of O_2 in Li^+ -containing organic electrolyte solutions can be summarized as depicted in eqs 13–16. Whether or not ORR ultimately leads to the formation of Li_2O_2 involving an overall two-electron reduction of O_2 or to the formation of Li_2O in a four-electron O_2 reduction depends on the conditions under which the electrochemistry is carried out. In cells in which the potential is scanned as in a cyclic voltammetry experiment, the three products LiO_2 , Li_2O_2 , and Li_2O can be selectively formed by controlling the potential at which the reduction is performed. In Li -air battery cells held under a constant supply of oxygen or air during its discharge, the main reaction product is Li_2O_2 , formed from the chemical decomposition of the initially formed $\text{Li}^+(\text{solvent})_n-\text{O}_2^-$, as shown in eq 14. The discharge product of the nonaqueous Li -air battery is well established to be Li_2O_2 .⁴¹



The superoxide being an anion radical is very reactive toward polar solvents and will react with many nonaqueous solvents. Organic carbonate solvents such as propylene carbonate have been shown to decompose in Li -air cells.^{41,45} The degree of reversibility revealed by the cyclic voltammograms of O_2 in organic electrolytes containing tetrabutyl ammonium salts can be used as a first-order measure to assess this reactivity.^{41,45} We have identified that organic sulfones and sulfoxides, especially dimethyl sulfoxide (DMSO), organic ethers such as poly-

ethylene glycol dimethyl ethers (PEGDMEs) with TEGDME as a prominent example, and room-temperature ionic liquids, exemplified by the two important candidates of 1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) and 1-methyl-1-butyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{PYR}_{14}\text{TFSI}$), are fairly stable solvents for use in the rechargeable Li -air battery.

Readers are referred to the work of Bruce et al.⁴⁵ on organic electrolyte stability and the O_2 reduction reaction mechanism, Shao Horn and co-workers⁴⁶ on the chemical and morphological changes in the Li/O_2 battery electrodes, and Nazar and co-workers⁴⁷ on the O_2 electrode catalysis for other recent contributions to the Li/O_2 battery cell chemistry.

The realization of a practical Li -air battery with long cycle life has remained elusive so far. The reasons for this are several, including the aforementioned degradation of the organic solvents as a result of their reactions with O_2 reduction products,^{41,45} passivation of the porous carbon electrode by the insulating discharge product Li_2O_2 and the associated poor rechargeability of the O_2 electrode,^{38–40} poor rechargeability of the Li anode,⁴¹ and contamination of the cell with impurities such as CO_2 and moisture when atmospheric O_2 is used as the cathode active material.

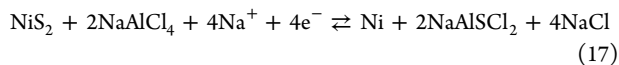
The development of a suitable barrier membrane on the cathode surface to prevent water and CO_2 from entering the cell is necessary in order to fully realize the practical potential of this rechargeable battery. Nevertheless, this author believes that practical Li -air batteries will be produced in the foreseeable future for strategic applications either as an ultrahigh energy density primary battery or as a rechargeable battery for short cycle life applications.

Rechargeable Li/Sulfur and Na/Metal Sulfide Batteries. A recent review by this author and colleagues has summarized the major advantages and disadvantages of the ambient-temperature Li/S battery and its state of development.⁴⁸ The concept of electrochemical energy conversion and storage utilizing sulfur as the positive electrode in an alkali metal anode battery dates back to the 1960s. Because of the insolubility of elemental S in organic electrolytes, early research focused on the use of lithium polysulfides (Li_2S_n) as soluble S cathodes.⁴⁹ The solubility of the polysulfides varies with the solvents used, and Li_2S_n in which n varies from 5 to 8 has been used to construct rechargeable Li cells.

The cycle life of the rechargeable Li/S battery utilizing the Li_2S_n cathode is limited by the solubility of the polysulfide in organic electrolytes and the ensuing sulfur shuttle reactions. Self-discharge and short cycle lives have served as impediments to the development of practical Li/S batteries utilizing liquid electrolytes in organic solvents such as tetrahydrofuran, methyl acetate, and dioxolane. Rechargeable cells incorporating a variety of polymer-containing electrolytes, including poly(ethylene oxide), PEGDME, and mixtures of PEGDME or tetraethylene glycol dimethoxyethane with ionic liquids, have shown longer cycle life and lower self-discharge. Pure ionic liquid electrolytes have also been utilized, but these cells suffered from rapid capacity fading. A composite cathode consisting of a MWCNT either as a MWCNT/ S nanocomposite with highly homogeneous sulfur dispersion or as a MWCNT core/sulfur shell structure, has shown better cycling stability with capacity utilization. Carbon/sulfur composites comprised of high pore volume carbons with 3D-accessible channel nanostructures have shown promise for improved cell performance. In these electrodes, sulfur is confined in the

interconnected pore structure of mesoporous carbon CMK-3. The use of Li^+ -conductive solid electrolytes such as $\text{Li}_2\text{S}-\text{SiS}_2$, $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, and lithiumaluminum titanium phosphate to isolate the anode from the cathode to prevent self-discharge and S shuttle reactions has been studied in Li/S cells. Recent progress in the cycle life of Li/S lab cells has been reported by Cui et al. using a new separator design,⁵⁰ Qiu et al. with a nitrogen-doped graphene-enabled sulfur electrode structure in a Li cell to yield about 2000 cycles,⁵¹ Lin and co-workers using sulfur-rich lithium polysulfidophosphate cathode,⁵² and Scrosati and co-workers in a Li ion cell configuration starting with a Li_2S cathode and a tin (Sn) anode in a solid polymer electrolyte cell.⁵³ Continued research addressing the challenges of S shuttle reactions and Li anode rechargeability would ultimately result in long cycle life rechargeable Li/S batteries.

My co-workers and I demonstrated several rechargeable Na batteries with metal sulfide cathodes operating in the moderately high temperature of 200 °C.⁵⁴ Specific examples include Na/NiS, Na/CuS, Na/FeS₂, and Na/NiS₂ batteries. In these batteries, the cathode is isolated from the anode by means of the Na^+ -conducting $\beta\text{-Al}_2\text{O}_3$ solid electrolyte separator. The cells have little self-discharge, and there is no sulfur shuttle. The reversible reactions of the NiS₂ cathode in the Na/NiS₂ cell involve the participation of the NaAlCl₄ electrolyte as shown in eq 17.



We demonstrated more than 600 full-depth charge/discharge cycles in this cell before the cycling was voluntarily terminated. Future studies involving these and other metal sulfides and oxides, either alone or in combination with metal halides, as cathodes are fertile areas for developing novel rechargeable Li and Na batteries.

Challenges to Develop Solid-State Lithium Batteries. All-solid-state batteries potentially offer a high degree of safety due to the absence of combustible organic solvents.⁵⁵ Traditionally, they have been fabricated as thin-film batteries in which the electrode and electrolyte layers have a micron to a few microns thickness. Recently, with the availability of highly conducting inorganic solid electrolytes with conductivities of 10^{-4} to 10^{-3} S/cm at room temperature,⁵⁶ attempts are being made to develop larger-capacity solid-state batteries as alternatives to traditional liquid-electrolyte-based Li systems while taking advantage of their superior safety characteristics. A case can be made for higher energy density (W h/L) in all-solid-state rechargeable lithium batteries for the following reasons: (i) the ability to insert and extract Li into and from layered metal oxide cathode materials over a wider voltage range, yielding higher capacities than possible in liquid electrolytes due to the wider voltage window of some solid electrolytes and (ii) the simplicity of all-solid-state lithium battery design, which can reduce the mass of inactive components to provide higher energy density compared with liquid-electrolyte-based batteries. In order to practically realize all-solid-state batteries with higher energy density than their liquid electrolyte counterparts, it would be necessary to overcome the high impedances associated with Li^+ transfer across solid electrolyte–solid electrode interfaces in them.

Another important requirement for high energy density solid-state Li batteries would be the ability to prepare a 40–60 μm thick composite cathode electrode from a powder mixture

of the solid electrolyte and active electrode material, similar to the electrodes in conventional Li ion batteries. The solid electrolyte in the composite electrode must be in intimate contact with the active electrode material, and the electrode should be as little porous as possible. These thick electrodes must exhibit discharge/charge rates comparable to that in liquid-electrolyte-based Li ion cells in order for the solid-state Li batteries to be practically viable substitutes for today's Li ion batteries. A schematic of an all-solid-state Li battery cell with the potential to achieve an energy density of >1000 W h/L is presented in Figure 9. It is comprised of a 40–60 μm thick

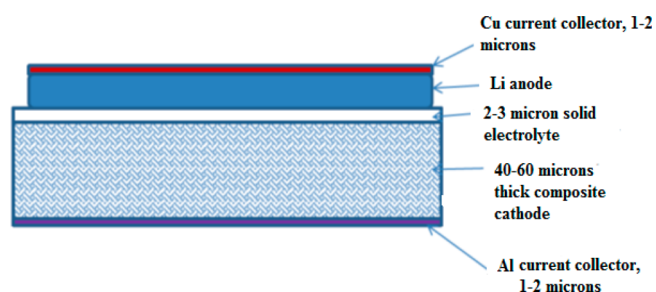


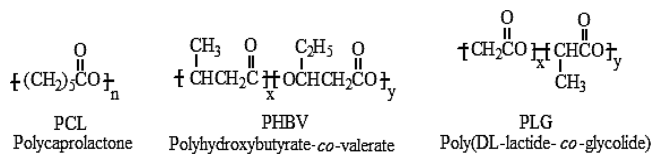
Figure 9. Conceptual design of an all-solid-state Li battery with >1000 W h/L.

composite metal dioxide cathode, a Li anode of matching thickness, and a 2–3 μm thick solid electrolyte. Several such battery cells will be series-connected in a bipolar configuration to form a battery pack that will minimize the amount of inactive packaging materials.

An advantage of the all-solid-state design is that it mitigates the leakage currents and self-discharge often encountered in bipolar series-connected battery packs utilizing liquid electrolytes. In order to realize high energy density from the all-solid-state Li battery, a Li metal anode that matches the thick cathode, shown in Figure 9, must be many microns thick. Such an anode will create substantial volume changes when the battery is discharged and charged. Thus, a major challenge of the development of high energy density all-solid-state Li batteries is to overcome the deleterious effects of volume changes on cell performance, particularly with respect to interfacial impedances and ion-transport rates. There has not yet been any breakthrough reported on such batteries in the open literature.

Biodegradable Batteries to Address Environmental Challenges. Growing environmental consciousness among the general consumers and impending crisis in landfill availability are expected to produce increased interest in developing biodegradable materials. Biodegradable batteries by virtue of the materials used to construct them are expected to be totally converted to carbon dioxide, water, and other trace inorganic products by the microorganisms present in the environment and by environmental factors such as light, moisture, and heat. In a preliminary study, we investigated the usefulness of three biodegradable polymers as hosts for gel polymer electrolytes.⁵⁷ They are poly(caprolactone) (PCL), poly(hydroxybutyrate-co-valerate) (PHBV), and poly(DL-lactide-co-glycolide) (PLG). They are polyesters in which the lone pair of electrons on the ester oxygen atoms should provide sufficient electron-donor power to solvate the Li^+ , leading to polymer electrolytes with ionic conductivity. The author and his colleague prepared these gel polymer electrolytes some time ago, but the results were not previously published. Gel polymer electrolytes with conductiv-

ities of about $10^{-3} \Omega^{-1} \text{ cm}^{-1}$ at room temperature and good mechanical strength were prepared from PHBV as the polymer host. We prepared gel polymer electrolyte membranes of about $80 \mu\text{m}$ thick in the following manner. The PHBV polymer was dissolved in methylene chloride, and the plasticizing solvent was then added, followed by the addition of an appropriate amount of the Li salt dissolved in acetonitrile. The resulting solution was cast on to a glass dish, and the solvents were evaporated to obtain free-standing polymer electrolyte films. The conductivities of the membranes were measured by means of impedance spectroscopy, as we previously reported.^{37,58}



PEGDMEs of molecular weights 250 and 500 (PEGDME 250 and PEGDME 500) or a mixed solvent of EC and PC were used to plasticize the PHBV-based polymer electrolytes utilizing either LiPF_6 or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ion-conducting salts. Of these polymer hosts, PHBV was found to be a good material to form gel polymer electrolytes of the following compositions with attractive room-temperature conductivities (K). The weight percentages (w/o) of the materials used to prepare each electrolyte membrane and their compositions are listed below:

- 37.3 w/o PHBV–6.7 w/o LiPF_6 –56 w/o EC/PC ($K = 1 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$)
- 35.4 w/o PHBV–11.6 w/o $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ –53 w/o EC/PC ($K = 6.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$)
- 27.2 w/o PHBV–4.9 w/o LiPF_6 –67.9 w/o PEGDME 500 ($K = 1 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$)
- 27.2 w/o PHBV–4.9 w/o LiPF_6 –67.9 w/o PEGDME 250 ($K = 2 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$)

The PHBV-based polymer electrolytes have an electrochemical stability window spanning the range of 0.0–4.0 V versus Li^+/Li , making them suitable for use in Li batteries and, in particular, for batteries with voltages as high as 4 V.

A Li/O_2 cell fabricated with PHBV-based polymer electrolytes as an example has an open-circuit voltage of 3 V and a load voltage lying between 2.3 and 2.5 V (Figure 10). The Li/O_2 cell was constructed, as we reported previously.³⁷ The versatility of the approach was demonstrated with the preparation of electrolytes from other biodegradable polymers,

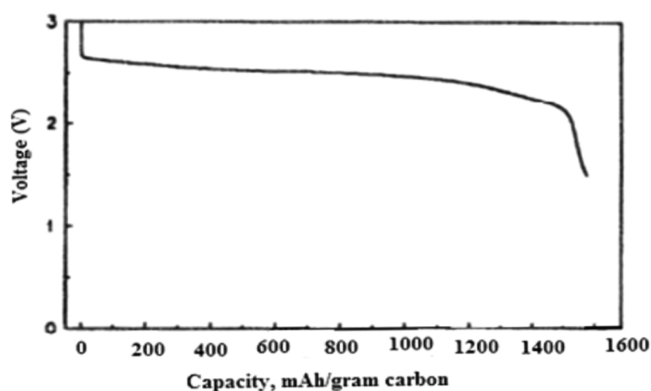


Figure 10. Discharge curve for a biodegradable Li/O_2 battery cell with a 37.3 w/o PHBV–6.7 w/o LiPF_6 –56 w/o EC/PC gel polymer electrolyte membrane. The discharge current density is $0.1 \text{ mA}/\text{cm}^2$.

such as PCL and PLG, and with the use of alternative plasticizers composed of PEGDMEs. These latter electrolytes would probably be more appropriate for rechargeable Li batteries.

The Li/O_2 primary battery depicted in Figure 10 was prepared with an organic carbonate-containing gel electrolyte in order to demonstrate feasibility of the approach. Rechargeable biodegradable Li/O_2 batteries would be built with electrolytes that are more stable in contact with their discharge products LiO_2 and Li_2O_2 .

It is anticipated that as the environmental consciousness of consumers continues to rise in the future, there will be increased efforts to prepare biodegradable electrolytes as well as active electrode materials for high energy density batteries. I hope that this account will spur interest in developing such batteries.

Challenge to Develop Low-Cost Batteries for Large-Scale Energy Storage. Large-scale electrochemical energy storage is not a new concept. Battery banks consisting of series and parallel stacked cells and modules leading to large-format batteries having kilowatts to megawatts of energy have been used in ships, telephone central stations, and electrical utility stations. In ships, torpedoes, and other naval vessels, batteries provide energy for starting, emergency power and auxiliary power for cabin lighting, navigation lighting, search light, navigation equipment, and many other activities. In telephone central stations, batteries provide backup power when electricity from power lines is lost, and in electric utility companies, battery banks are used for power management functions, including power conditioning, load-leveling, frequency regulation, power plant hybridization, as well as many other power generation and distribution functions. Traditionally, aqueous lead–acid and Ni–Cd batteries have been used for large-scale energy storage. They are relatively inexpensive batteries that meet the price requirements of utilities, but they are high-maintenance systems with a relatively short cycle life. With increasing growth of solar and wind power, new high energy density, and low cost, batteries to store the energy from them is becoming a serious challenge. Alternative high energy density batteries being developed include the rechargeable Na batteries with sulfur and metal chloride/metal sulfide cathodes discussed earlier and aqueous and nonaqueous redox flow batteries.^{59,60} Some of the redox flow batteries under development include zinc–bromine, iron–chromium, and all-vanadium redox flow systems and a nonmetal redox flow battery based on the organic negative electrode of the quinone–quinonoid and the positive electrode of bromine–bromide redox couples.^{59,60} Li ion batteries such as the C/LiFePO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$, and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li-Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ batteries characterized by the very long cycle life of many thousands of cycles at 1C–10C rates and good safety characteristics are also the focus of development efforts. Although the initial cost of these Li ion batteries is high, their lifetime cost will be lower due to the very long cycle life. However, the cost of Li ion batteries will continue to be a challenge until superior low-cost electrode and electrolyte materials are developed to address this issue.

Advanced Nonaqueous Electrolytes for Lithium Batteries: The Liquid to Polymer Electrolyte Continuum. Electrolytes play a central role in the performance of Li batteries irrespective of whether they are based on intercalation or displacement reaction electrodes. The operational and storage temperature windows of Li ion batteries to a large extent are constrained by the liquid electrolyte that they contain. At moderately high

temperatures (e.g., 50–85 °C), decomposition of organic liquid electrolyte is a limiting factor in Li ion batteries, while at low temperatures (e.g., –20 to –50 °C), decrease in solution conductivity and Li salt solubility contribute to reduction in or lack of performance.

The conductivity versus temperature profiles of Li⁺-conducting electrolytes may be used as a useful tool to search for new electrolytes with improved low-temperature performance. We showed that liquid electrolytes comprising Li salts dissolved in organic solvents do not generally exhibit a linear behavior in the logarithm of conductivity (κ) versus reciprocal absolute temperature plot within the temperature range of –40 to +80 °C. That means that the effect of temperature on conductivity cannot be described by the activation mechanism mathematically expressed as the Arrhenius law defined by eq 18

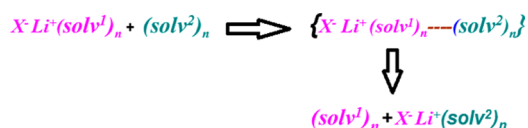
$$\kappa = \kappa_0 \exp\left(-\frac{E_a}{RT}\right) \quad (18)$$

where, κ_0 is a constant, E_a is the activation energy for the ion's motion in solution, and R and T are the gas constant and absolute temperature, respectively. The conductivity–temperature behavior is more accurately expressed by the Vogel–Tammann–Fulcher (VTF) relation shown in eq 19^{61,62}

$$\kappa = AT^{-1/2} \exp\left(-\frac{B}{T - T_0}\right) \quad (19)$$

where, A , B , and T_0 are constants. Although the exponential term looks similar to that in the Arrhenius equation, the B term does not have the same meaning of activation energy. Here, B is related to the activation energy for the creation of critical free volume for ion transport, and T_0 is the temperature at which the transport function ceases to exist or the solvent structural relaxation becomes zero and may be considered as the glass transition temperature, T_g , or a temperature near it. During ion conduction, the moving ion may either haul a portion of its solvation sheath with it or form a new solvation sheath in a new location, or both. The result is that the composition of the solvent in the ion's solvent coordination sphere would change as it moves from one site to the next. In other words, the motion of the ions from one coordination site (solv^1) to another (solv^2) is assisted by the motion of the solvent, as depicted in Scheme 4. The VTF ion conduction mechanism

Scheme 4. A Schematic Representation of Ion Transport via a Solvent-Coupled Motion Mechanism in Liquid Electrolytes in Which Ion Movement Is Assisted by the Motion of Solvent Molecules



illustrated in Scheme 4 may be used to elucidate the factors affecting ion conduction in nonaqueous electrolytes and to design electrolyte compositions for improved low-temperature performance.

Low-temperature performance of Li ion batteries is important because many parts of North America and Europe encounter winter month temperatures as low as –30 °C or lower. My colleagues and I have shown that an approach to prepare liquid electrolytes with improved low-temperature

performance is to use electrolytes composed of mixed solvents as they form Li salt solvates with lower melting points at certain ratios of the solvents and the Li salt in the mixture. Another strategy used to improve the low-temperature conductivity of liquid electrolytes is to use low-viscosity solvents either alone or mixed with higher viscosity electrolytes. The data in Figure 11

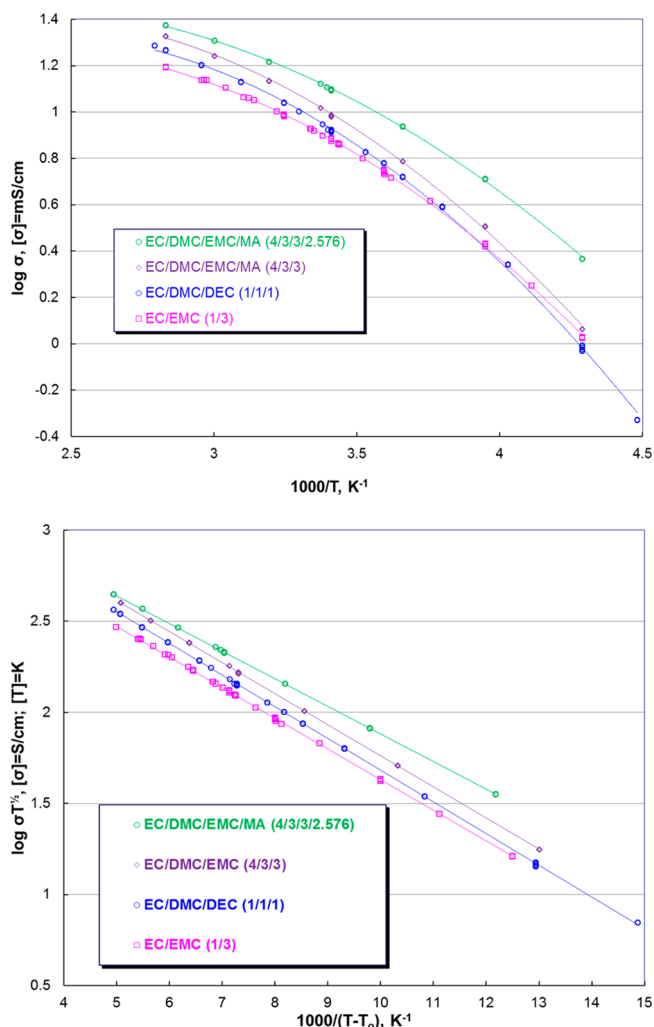


Figure 11. Conductivity versus temperature of several Li ion battery electrolytes plotted in the Arrhenius (above) and VTF (below) coordinates. The four mixed solvent-based electrolytes were prepared from 1 M LiPF₆ in various volume ratios of EC, DMC, DEC, EMC, and methyl acetate (MA) to achieve improved low-temperature conductivity. The volume ratios of the solvents for each electrolyte are indicated in the inset in the graph. The T_0 values for the electrolytes from top to bottom in the figures are 151, 156, 156, and 153 K (these data were collected by the author with his former colleague Boris Ravdel of Yardney Technical Products, RI).

depict the improved low-temperature conductivity of Li ion battery electrolytes prepared with the addition of various low-viscosity solvents to EC-based electrolytes. The conductivity data for these electrolytes plotted in the Arrhenius and VTF forms shown in Figure 11 illustrate that the Li ion transport is consistent with the solvent-assisted VTF mechanism illustrated in Scheme 4, and the values of T_0 , which are close to the T_g are probably good measures of their low-temperature performance. In general, electrolytes with lower T_g would exhibit better low-temperature performance. The T_0 values given in Figure 11,

consistent with their superior low-temperature conductivities, are lower than those for any electrolytes that we previously reported.^{61,62}

We have found that that not only do organic solid polymer electrolytes but also organic gel polymer electrolytes and liquid electrolytes conform to the VTF conductivity mechanism, thus exhibiting a continuum in the conductivity–temperature behavior of Li ion battery electrolytes. In these three classes of electrolyte ionic conduction occurs at temperature above T_g , where the ionic motion is coupled to the mobility of the solvent (polymer) molecules. On the other hand, in the inorganic solid electrolytes discussed in the previous section, conductivity occurs below the glass transition temperature, where the ionic motion is decoupled from the motion of the solid electrolyte crystal lattice. Identifying functional electrolytes with superior low-temperature performance and a wider voltage window will continue to remain a challenge in the development of rechargeable Li batteries.

Summary and Future Outlook. Li ion batteries have contributed immensely to shape the modern world by being the indispensable power source of choice for portable data and voice communication devices and long-range electric automobiles. There is an ever increasing need for rechargeable batteries with significantly higher energy and power densities in order to meet the growing demands for portable consumer devices with advanced functionalities, long-range electric automobiles, aerospace vehicles, improved power tools, low-cost electricity storage in utilities, and many other energy-hungry applications.

Ultimately, there is a limit in the energy density of energy storage systems that can be developed via electrochemical reactions.

The energy densities of Li ion batteries have reached a level of maturity, with the result that significant challenges are anticipated in the development of significantly higher energy density batteries. The specific capacities of cathode active materials limit the energy densities of rechargeable batteries because metallic Li or its alloys with Si, Sn, and other metals can provide high-capacity anodes. New Li battery chemical couples with low equivalent weights and high voltages must be sought to produce ultrahigh energy density rechargeable batteries. Such batteries include Li/O₂, Li/S, Li/metal halide, and Li/metal oxide systems in which the electrode processes involve displacement reactions accompanied by bond breaking among their constituent elements. Achieving a long cycle life in batteries using such electrode materials remains a major challenge. Future development of advanced battery materials and systems should also include all-solid-state batteries with performance similar to that of their liquid electrolyte counterparts to produce safer batteries, biodegradable batteries to address environmental challenges, low-cost batteries with long cycle life for large-scale energy storage and long-range electric automobiles, and consideration of the liquid to polymer electrolyte continuum for preparing advanced electrolytes for Li batteries.

AUTHOR INFORMATION

Corresponding Author

*E-mail: kmabraham@comcast.net.

Notes

The authors declare no competing financial interest.

Biography

Dr. K. M. Abraham is research professor at Northeastern University and principal of E-KEM Sciences (www.e-kemsciences.com). He has published over 200 scientific papers and holds 16 U.S. patents on advanced batteries. He is the recipient of The Electrochemical Society Battery Research Award and NASA Group Achievement Award for Rechargeable Lithium Battery Team.

ACKNOWLEDGMENTS

The author acknowledges the valuable contributions of all of his past and present co-workers whose names appear in the various references cited in this Perspective.

REFERENCES

- (1) 101 Gadgets That Changed The World. <http://www.popularmechanics.com/technology/gadgets/reviews/101-gadgets-that-changed-the-world#slide-101> (2014).
- (2) Linden, D.; Reddy, T. R. *Handbook of Batteries*, 4th ed.; McGraw Hill: New York, 2011; Chapter 26.
- (3) Dahn, J. R.; Sleigh, A. K.; Shi, H.; Way, B. M.; Weydanz, W. J.; Reimers, J. N.; Zhong, Q.; Von Sacken, U. In *Lithium Batteries*; Pistoia, G., Ed.; Elsevier: New York, 1994; Chapter 1.
- (4) Scrosati, B.; Abraham, K. M.; Van Schalkwijk, W.; Hassoun, J. *Lithium Batteries: Advanced Technologies and Applications*; John Wiley and Sons: Hoboken, NJ, 2013.
- (5) Winter, M.; Besenhard, J. O.; Spahr, M. E.; Novak, P. Insertion Electrode Materials for Rechargeable Lithium Batteries. *Adv. Mater.* **1998**, *10*, 725–763.
- (6) Shah, A.; Ates, M. N.; Kotz, S.; Seo, J.; Abraham, K. M.; Somu, S.; Busnaina, A. A. Layered Carbon Nanotube Architecture for High Power Lithium Ion Batteries. *J. Electrochem. Soc.* **2014**, *161*, A989–A995.
- (7) Bruce, P.; Scrosati, B.; Tarascon, J.-M. Nanomaterials for Rechargeable Lithium Batteries. *Angew. Chem., Int. Ed.* **2008**, *47*, 2930–2946.
- (8) Prossini, P.; Lisi, M.; Zane, D.; Pasquali, M. Determination of the Chemical Diffusion Coefficient of Lithium in LiFePO₄. *Solid State Ionics.* **2002**, *148*, 45–51.
- (9) Bazant, M. Z. Theory of Chemical Kinetics and Charge Transfer Based on Non-equilibrium Thermodynamics. *Acc. Chem. Res.* **2013**, *46*, 1144–1160.
- (10) Campion, C. L.; Li, W.; Euler, W. B.; Lucht, B. L.; Ravidel, B.; DiCarlo, J. F.; Gitzendanner, R.; Abraham, K. M. Suppression of Toxic Compounds Produced in the Decomposition of Lithium-Ion Battery Electrolytes. *Electrochem. Solid-State Lett.* **2004**, *7*, A194–A197.
- (11) Jow, T. R.; Zhang, S.; Xu, K.; Ding, M. Non-aqueous Electrolyte Solutions Comprising Additives and Non-aqueous Electrolyte Cells Comprising the Same. U.S. Patent 6905762, 2005.
- (12) Abraham, K. M.; Pasquariello, D. M.; Willstaedt, E. B. J. n-Butylferrocene for Overcharge Protection of Secondary Lithium Batteries. *J. Electrochem. Soc.* **1990**, *137*, 1856–1857.
- (13) Yoshimoto, N.; Niida, Y.; Egashira, M.; Morita, M. Nonflammable Gel Electrolyte Containing Alkyl Phosphate for Rechargeable Lithium Batteries. *J. Power Sources.* **2006**, *163*, 238–242.
- (14) Feng, J. K.; Ai, X. P.; Cao, Y. L.; Yang, H. X. A Highly Soluble Dimethoxybenzene Derivative as a Redox Shuttle for Overcharge Protection of Secondary Lithium Batteries. *Electrochem. Commun.* **2007**, *9*, 25–30.
- (15) Xu, M.; Dalavi, S.; Lucht, B. L. In *Lithium Batteries: Advanced Technologies and Applications*; Scrosati, B., Abraham, K. M., Van Schalkwijk, W., Hassoun, J., Eds.; John Wiley and Sons: Hoboken, NJ, 2013; Chapter 4.
- (16) Wilken, S.; Johansson, P.; Jacobsson, P. In *Lithium Batteries: Advanced Technologies and Applications*; Scrosati, B., Abraham, K. M.,

Van Schalkwijk, W.; Hassoun, J., Eds.; John Wiley and Sons: Hoboken, NJ, 2013; Chapter 3.

(17) Abraham, K. M.; Pasquariello, D.; Willstaedt, E. M. Discharge Rate Capability of the LiCoO₂ Electrode. *J. Electrochem. Soc.* **1998**, *145*, 482–486.

(18) Johnson, Z.; Cordova, S.; Abraham, K. M. High Power Lithium Ion Battery Facilitated by an Advanced Cathode. *Proceedings of the Meeting of Society of Automotive Engineers (SAE)* **2008**, DOI: 10.4271/2008-01-2866.

(19) Ragone, D. V. Theory of Ragone Plots. *Proceedings of the Meeting of Society of Automotive Engineers (SAE)* **1968**, paper 80453.

(20) Blomgren, G. E. Electrolytes for Advanced Batteries. *J. Power Sources* **1999**, *81–82*, 112–118.

(21) Thomas, K. E.; Darling, R. M.; Newman, J. *Advances in Lithium-Ion Batteries*; Kluwer Academic/Plenum Publishers: New York, 2002; pp 345–392.

(22) Santhanagopalan, S.; Gu, Q.; Ramadass, P.; White, R. Review of Models for Predicting the Cycling Performance of Lithium Ion Batteries. *J. Power Sources* **2006**, *156*, 620–628.

(23) Al-Hallaj, S.; Selman, J. R.; Dinwiddie, R. B.; Wang, H. Thermal Properties of Lithium-Ion Battery and Components. *J. Electrochem. Soc.* **1999**, *146*, 947–954.

(24) Smart, M. C.; Ratnakumar, B. V.; Ryan-Mowrey, V. S.; Surampudi, S.; Prakash, G. K. S.; Hub, J.; Cheung, I. Improved Performance of Lithium-Ion Cells with the Use of Fluorinated Carbonate-Based Electrolytes. *J. Power Sources* **2003**, *119–121*, 359–367.

(25) Zhang, S. A. Review on Electrolyte Additives for Lithium-Ion Batteries. *J. Power Sources* **2006**, *162*, 1379–1394.

(26) Abraham, K. M. Rechargeable Batteries for the 300-Mile Electric Vehicle and Beyond. *ECS Trans.* **2012**, *41*, 27–34.

(27) Lu, Z.; MacNeil, D. D.; Dahn, J. R. Layered Li[Ni_xCo_{1–2x}Mn_x]-O₂ Cathode Materials for Lithium-Ion Batteries. *Electrochem. Solid-State Lett.* **2001**, *4*, A191–A194.

(28) (a) Ates, M. N.; Mukerjee, S.; Abraham, K. M. A Li-Rich Layered Cathode Material with Enhanced Structural Stability and Rate Capability for Li-Ion Batteries. *J. Electrochem. Soc.* **2014**, *161*, A355–A363. (b) See also: Ates, M. N.; Jia, Q.; Shah, A.; Busnaina, A.; Mukerjee, S.; Abraham, K. M. Mitigation of Layered to Spinel Conversion of a Li-Rich Layered Metal Oxide Cathode Material for Li-Ion Batteries. *J. Electrochem. Soc.* **2014**, *161*, A290–A301.

(29) Allen, C. J.; Jia, Q.; Chinnasamy, C. N.; Mukerjee, S.; Abraham, K. M. Synthesis, Structure and Electrochemistry of Lithium Vanadium Phosphate Cathode Materials. *J. Electrochem. Soc.* **2011**, *158*, A1250–A1259.

(30) Ellis, B. L.; Makahnouk, W. R. M.; Makimura, Y.; Toghiani, K.; Nazar, L. F. A Multifunctional 3.5 V Iron-based Phosphate Cathode for Rechargeable Batteries. *Nat. Mater.* **2007**, *6*, 749–753.

(31) Recham, N.; Chotard, J. N.; Dupont, L.; Delacourt, C.; Walker, W.; Armand, M.; Tarascon, J. M. A 3.6 V Lithium-Based Fluorosulphate Insertion Positive Electrode for Lithium-Ion Batteries. *Nat. Mater.* **2010**, *9*, 68–74.

(32) Yang, J.; Kang, X.; Hu, L.; Gong, X.; Mu, S. Nanocrystalline-Li₂FeSiO₄ Synthesized by Carbon Frameworks as an Advanced Cathode Material for Li-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 6870–6878.

(33) Badway, F.; Cosandey, F.; Pereira, N.; Amatucci, G. G. Carbon Metal Fluoride Nanocomposites High-Capacity Reversible Metal Fluoride Conversion Materials as Rechargeable Positive Electrodes for Li Batteries. *J. Electrochem. Soc.* **2003**, *150*, A1318–A1327.

(34) Cabana, J.; Monconduit, L.; Larcher, D.; Palacin, M. Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions. *Adv. Mater.* **2010**, *22*, E170–E192.

(35) Lin, F.; Nordlund, D.; Weng, T.; Zhu, Y.; Ban, C.; Richards, R. M.; Xin, X. L. Phase Evolution for Conversion Reaction Electrodes in Lithium-Ion Batteries. *Nat. Commun.* **2014**, *5*, 3358–3362.

(36) Amatucci, G. G.; Pereira, N. Fluoride-Based Electrode Materials for Advanced Energy Storage Devices. *J. Fluorine Chem.* **2007**, *128*, 243–262.

(37) Abraham, K. M.; Z. Jiang, J. A Polymer Electrolyte-Based Rechargeable Lithium/Oxygen Battery. *J. Electrochem. Soc.* **1996**, *143*, 1–5.

(38) Girishkumar, G.; McCloskey, B.; Luntz, A. C.; Swanson, S.; Wilcke, W. Lithium–Air Battery: Promise and Challenges. *J. Phys. Chem. Lett.* **2010**, *1*, 2193–2203.

(39) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J.-M. Li–O₂ and Li–S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19–29.

(40) Christensen, J.; Albertus, P.; Sanchez-Carrera, R. S.; Lohmann, T.; Kozinsky, B.; Liedtke, R.; Ahmed, J.; Kojic, A. A Critical Review of Li/Air Batteries. *J. Electrochem. Soc.* **2012**, *159*, R1–R30.

(41) Abraham, K. M. Electrolyte-Directed Reactions of the Oxygen Electrode in Lithium–Air Batteries. *J. Electrochem. Soc.* **2014**, *162*, A3021–A3031.

(42) Laoire, C. O.; Mukerjee, S.; Abraham, K. M.; Plichta, E. J.; Hendrickson, M. A. Influence of Non-aqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium–Air Battery. *J. Phys. Chem. C* **2010**, *114*, 9178–9186.

(43) Allen, C. J.; Hwang, J.; Kautz, R.; Mukerjee, S.; Plichta, E. J.; Hendrickson, M. A.; Abraham, K. M. Oxygen Reduction Reactions in Ionic Liquids and the Formulation of a General ORR Mechanism for Li–Air Batteries. *J. Phys. Chem. C* **2012**, *116*, 20755.

(44) Allen, C. J.; Mukerjee, S.; Plichta, E. J.; Hendrickson, M. A.; Abraham, K. M. Oxygen Electrode Rechargeability in an Ionic Liquid for the Li–Air Battery. *J. Phys. Chem. Lett.* **2011**, *2*, 2420.

(45) Johnson, L.; Li, C.; Liu, Z.; Chen, Y.; Freunberger, S. A.; Ashok, P. C.; Praveen, B. B.; Dholakia, K.; Tarascon, J. M.; Bruce, P. G. The Role of LiO₂ Solubility in Aprotic Solvents and Its Consequences for Li–O₂ Batteries. *Nat. Chem.* **2014**, *6*, 1091–1099.

(46) Gallant, B. M.; Mitchell, R. R.; Kwabi, D. G.; Zhou, J.; Zuin, L.; Thompson, C. V.; Shao-Horn, Y. Chemical and Morphological Changes of Li–O₂ Battery Electrodes Upon Cycling. *J. Phys. Chem. C* **2012**, *116*, 20800–20805.

(47) Black, R.; Lee, J.-H.; Adams, B.; Mims, C. A.; Nazar, L. F. The Role of Catalysts and Peroxide Oxidation in Lithium–Oxygen Batteries. *Angew. Chem., Int. Ed.* **2013**, *52*, 392–396.

(48) Bruce, P. G.; Hardwick, L. J.; Abraham, K. M. Lithium–Air and Lithium–Sulfur Batteries. *Mater. Res. Soc. Bull.* **2011**, *36*, 506–512.

(49) Rauh, R. D.; Abraham, K. M.; Pearson, G. F.; Surprenant, J. K.; Brummer, S. B. A Lithium/Dissolved Sulfur Battery with an Organic Electrolyte. *J. Electrochem. Soc.* **1979**, *126*, S23–S27.

(50) Yao, H.; Yan, K.; Li, W.; Zheng, G.; Kong, D.; Seh, W. Z.; Narasimhan, V. K.; Liang, Z.; Cui, Y. Improved Lithium–Sulfur Batteries with a Conductive Coating on the Separator. *Energy Environ. Sci.* **2014**, *7*, 3381–3390.

(51) Qiu, Y.; Li, W.; Zhao, Z.; Li, G.; Liu, M.; Zhou, L.; Li, H.; Wei, Z.; Yang, S.; Duan, W.; Ye, Y.; Guo, J.; Zhang, Q. High-Rate, Ultralong Cycle-Life Lithium/Sulfur Batteries Enabled by Nitrogen-Doped Graphene. *Nano Lett.* **2014**, *14*, 4821–4827.

(52) Lin, Z.; Liu, Z.; Fu, W.; Dudney, N. Lithium Polysulfidophosphates: A Family of Lithium-Conducting Sulfur-Rich Compounds for Lithium–Sulfur Batteries. *Angew. Chem., Int. Ed.* **2013**, *52*, 7460–7463.

(53) Hassoun, J.; Scrosati, B. Moving to a Solid-State Configuration: A Valid Approach to Making Lithium–Sulfur Batteries Viable for Practical Applications. *Adv. Mater.* **2010**, *22*, 5198–5201.

(54) Abraham, K. M.; Elliot, J. E. Moderate Temperature Sodium Cells. *J. Electrochem. Soc.* **1984**, *131*, 2211–2217.

(55) Dudney, N. J. Solid-State Thin-Film Rechargeable Batteries. *Mater. Sci. Eng.* **2005**, *B 116*, 245.

(56) Kamaya, N.; Homma, K.; Yamakawa, Y.; Hirayama, M.; Kanno, R.; Yonemura, M.; Kamiyama, T.; Kato, Y.; Hama, S.; Kawamoto, K.; Mitsui, A. A Lithium Superionic Conductor. *Nat. Mater.* **2011**, *10*, 682–686.

(57) Karlsson, S.; Albertsson, A. Biodegradable Polymers and Environmental Interaction. *Polym. Eng. Sci.* **1998**, *38*, 1251–1253.

(58) Choe, H. S.; Carroll, B. G.; Pasquariello, D. M.; Abraham, K. M. Characterization of Some Polyacrylonitrile- Based Electrolytes. *Chem. Mater.* **1997**, *9*, 369–379.

(59) Huskinson, B.; Marshak, M. P.; Suh, C.; Er, S.; Gerhardt, M. R.; Galvin, C. J.; Chen, X.; Aspuru-Guzik, A.; Gordon, R. G.; Aziz, M. J. A Metal-Free Organic–Inorganic Aqueous Flow Battery. *Nature* **2014**, *505*, 195–198.

(60) Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334*, 928–35.

(61) Gu, G. Y.; Laura, R.; Abraham, K. M. Conductivity–Temperature Behavior of Organic Electrolytes. *Electrochem. Solid-State Lett.* **1999**, *2*, 486–489.

(62) Gu, G. Y.; Laura, R.; Rzeznik, M.; Abraham, K. M. 2-Methoxyethyl (Methyl) Carbonate-Based Electrolytes for Li-Ion Batteries. *Electrochim. Acta* **2000**, *4*, 3127–39.