# Lithium-Ion Batteries: Thermomechanics, Performance, and Design Optimization

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## 1   INTRODUCTION

Given the need to reduce environmental impact and to enhance energy security, an increasing emphasis is being placed on renewable energy sources. One of the key technologies in leveraging renewable energy sources in transportation is the lithium-ion battery. The current lithium-ion technology market size is approximately US$11 billion, and given the growing demand from a number of sectors, it is expected to triple in the next 5 years.

Lithium-ion batteries have not only become the energy-storage system (ESS) of choice for a variety of portable electronic devices, but they are also being increasingly used in hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) to displace fossil fuels. Other key applications of lithium-ion batteries include aviation (Traub, 2011), satellites (Fellner *et al.*, 2003), and grid storage (Du, Garcia, and Paredis, 2014). As shown in Table 1, lithium-ion batteries have important properties that can benefit different applications, but they must also be capable of meeting a wide range of design and operational requirements.

While lithium-ion batteries have been commercialized for over 20 years, interest in lithium-ion-related research has not diminished as the government and the private sectors alike continue to work toward lithium-ion batteries with higher performance and better safety. This article provides a brief summary of the various aspects of lithium-ion battery technology, starting with an overview of the battery system. This overview is followed by a description of the battery components and the different types of lithium-ion batteries. Recent advances in modeling and design, especially in thermomechanical modeling, design optimization, and performance improvement, are highlighted, along with a discussion of the challenges involved in further lithium-ion battery development.

## 2   FUNDAMENTALS OF LITHIUM-ION BATTERIES

A battery is an electrochemical device that converts stored chemical energy into electrical energy via the energy difference between the reactions occurring at the two electrodes. A number of elementary cells may be stacked in series or in parallel to provide the required voltage or power. The amount of energy and power available is a function of the energy-storage materials in the electrodes and the standard potential difference between the reactions. Most lithium-ion batteries such as those used in electric vehicles are rechargeable or secondary batteries that shuttle $Li^+$ ions back and forth between the two electrodes. Lithium is favored as the shuttling ion for a battery as it is the most electropositive (standard electrode potential = 3.04 V) and the lightest metal (equivalent mass = 6.94 g/mol), both of which are essential for high energy density (Haynes, Lide, and Bruno, 2012). The lithium-based rechargeable battery was first demonstrated in the 1970s using lithium metal as

the negative electrode and titanium sulfide as the positive electrode (Whittingham, 1976). This pioneering battery system was found to have poor cycling behavior, as dendritic growth due to lithium plating on repeated cycling could result in short-circuiting and explosion. Lithium metal was subsequently replaced by a second insertion material as the negative electrode to avoid lithium plating problems (Murphy *et al.*, 1978). The lithium-ion battery operates by incorporating lithium into the active material via a process in which the ions are reversibly removed or inserted into a porous host without significantly changing its structure. The family of metal oxide compounds of the form $Li_xMO_2$ (where "M" represents Co, Ni, or Mn) was proposed in the 1980s (Mizushima *et al.*, 1980; Thackeray *et al.*, 1983) and has since gained widespread acceptance as the standard active material in cathodes.

Lithium-ion batteries were first commercialized in 1991 by Sony Corporation, and have since been used to power an increasing variety of appliances. Compared to the previous generations of rechargeable batteries, such as lead-acid, nickel-cadmium (Ni-Cd), and nickel metal-hydride (Ni-MH), lithium-ion batteries have higher energy and power density (Figure 1). In addition, they exhibit high rate capability, broad operating temperature range, low self-discharge, and no memory effects (Linden and Reddy, 2002). However, they are more expensive and less tolerant to abuse. More importantly, the energy density of lithium-ion batteries is still more than one order of magnitude lower

**Table 1.** Applications of lithium-ion batteries.

| Application | Benefits of Li-Ion Batteries | Unique Challenges |
|---|---|---|
| Electronics | Low volume, high capacity | Abuse tolerance, safety |
| Automotive | Low weight and volume, high energy and power density | Cycle and calendar life, fast charging, safety |
| Aviation | Low weight and volume, high energy and power density | Scalability, fast charging, safety |
| Spacecraft | Low weight and volume, high energy density | Sensitivity to extreme temperatures and radiation |
| Grid | Low self-discharge, high efficiency | Scalability, cost |

than that of fuels such as gasoline, resulting in either limited range or expensive and bulky battery packs in electric vehicles (EVs). Much of the ongoing research efforts on lithium-ion batteries are focused on reducing cost and increasing energy density.

Lithium-ion batteries are produced in a variety of formats, the most common of which are the cylindrical (18650 form) and prismatic formats. A typical cell consists of two insertion electrodes that allow reversible insertion and extraction of lithium ions. The negative electrode (also known as *anode*) is typically a carbon-based material, whereas the positive electrode (cathode) consists of a lithium metal oxide. The
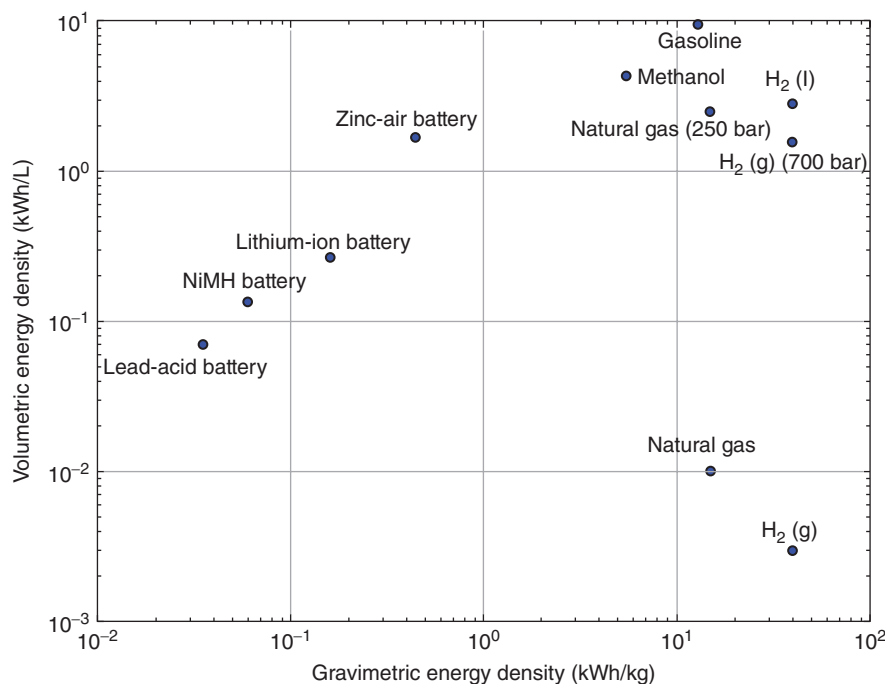


**Figure 1.** Energy density comparison of various energy-storage systems. *Source*: Reproduced with permission from Du, 2013. © W. Du.

electrodes are coated onto a metal foil current collector (Al for cathode and Cu for anode) with a binder, usually polyvinylidene fluoride (PVDF). The insertion electrodes are electrically nonconductive, requiring the addition of a conductive agent, which is usually achieved with high surface-area carbon particles to facilitate electron movement along the surface of the active material. A separator between the two electrodes prevents them from coming into direct contact and short-circuiting. The separator is normally a polyethylene or a polypropylene separator film that is semipermeable. The cell is immersed in a liquid electrolyte that consists of a lithium salt—such as $LiPF_6$—dissolved in organic solvents to provide ion transfer between the electrodes. Alternatives such as gel-polymer and solid-state electrolytes can be used, depending on the application and safety and life cycle requirements.

In its simplest form, a cell consists of current collectors, electrodes, electrolyte, a separator, and numerous inactive materials, such as binders and conductive additives, to enhance critical physical properties of the cell. On discharge, electrons are extracted from the anode via the current collector, and at the same time, lithium ions move from the anode into the electrolyte and migrate toward the cathode. At the cathode side, the electrons from the external circuit enter the cathode via the positive current collector. These electrons combine with the migrated lithium ions that are inserted into the active material solid matrix. On charge, the reactions are reversed by applying a voltage to the external circuit, and the lithium ions are extracted from the cathode and inserted back into the anode. The overall reaction can be shown as:

$$LiMO_2 + C \iff Li_xC + Li_{1-x}MO_2$$
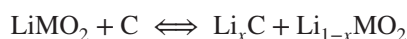
The Coulombic charge capacities of the active materials and the standard potential difference between the cathodic and anodic reactions determine the amount of energy that can be stored in a cell. Therefore, the maximum energy density is mainly a function of the electrode material properties, although in the later section, we will see that cell design plays an important role in determining how much of the theoretical total energy can be utilized during cycling. The choice of transition metal compound for the cathode is a key design consideration, as different compounds exhibit significant differences in charge capacity and standard potential resulting from their crystal lattice structures. Transition metal oxides can have a layered structure such as $LiCoO_2$, a spinel structure such as $LiMn_2O_4$, or an olivine-type phase structure such as in $LiFePO_4$, each of which has unique cycling characteristics (Whittingham, 2004). Table 2 lists properties of the most common cathode materials.

**Table 2.** Theoretical performance limits of common cathode properties materials.

| Cathode Material | Energy Density | | Coulombic Capacity (mAh/g) |
| --- | --- | --- | --- |
| | Wh/L | Wh/kg | |
| $Li_xMn_2O_4$ | 2060 | 490 | 120 |
| $Li_xFePO_4$ | 2070 | 580 | 170 |
| $Li_xV_2O_5$ | 2920 | 870 | 360 |
| $Li_xCO_2$ | 3000 | 600 | 150 |
| $Li_x(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ | 3680 | 770 | 200 |
| $Li_x(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ | 3780 | 740 | 190 |

*Source*: Created by the author using data from Sastry, 2014.

In the continued search for higher performance batteries, considerable ongoing research remains focused on the development of new electrode materials with superior capacity and electrical potential. A detailed discussion of specific developments in lithium-ion battery materials is beyond the scope of this article, but interested readers can find such discussions in recent review articles by Etacheri *et al*. (2011) and Marom *et al*. (2011).

## 3 CELL OPERATION

The performance of a cell is given by the open-circuit voltage (OCV) curve, plotted either as a function of the state of charge (SOC) or as a function of the depth of discharge (DOD). The OCV of a full cell is the resultant potential difference between the anode and the cathode OCVs, as shown in Figure 2. The OCV determines the maximum energy that can be extracted per electron during cell cycling. In reality, the voltage obtainable on discharge is always less than the OCV, as the internal resistance in the cell causes a voltage drop when current passes through the cell. The voltage drop in the cell is approximately proportional to the current.

As the current passing through the cell increases, the power increases, and the available discharge capacity decreases owing to inefficient utilization. Therefore, one can see that there is a trade-off between energy and power in the cell. The resulting power versus energy curve is called a *Ragone plot*, an example of which is shown in Figure 3. The end points of the Ragone plot indicate the maximum achievable energy density and power density for a given cell. The shape of the curve depends on the electrode material properties, such as OCV shape and Coulombic capacity of the active materials. At the same time, cell design and construction play an important role in determining the cycling performance of the cell, as shown by the difference between the Ragone plots of the two different lithium cobalt oxide cells. Therefore, it is imperative that an appropriate type of cell is chosen for a given application.
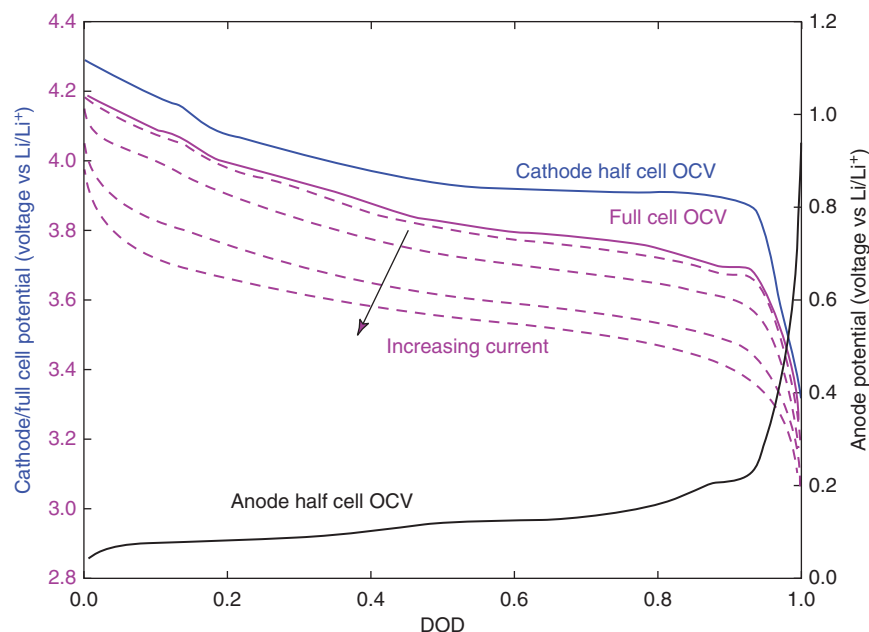
**Figure 2.** Voltage variations of a lithium cobalt oxide cell with discharge current based on experimental measurements.
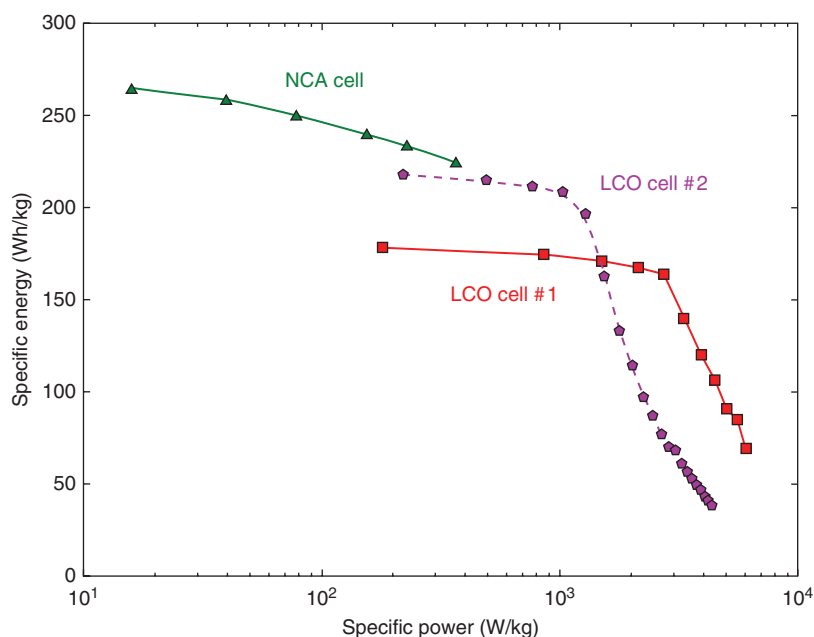


**Figure 3.** Ragone plots based on simulations of different types of lithium-ion cells.

# 4   MODELING OF LITHIUM-ION BATTERIES

As in many subjects, research and development approaches for lithium-ion batteries can be broadly separated into theoretical and experimental. Experimental work is of critical importance in the early phases of new technology, as methods for characterization and testing are needed to help gain a basic understanding of the relevant physical phenomena and establish guidelines for design and manufacturing. For lithium-ion batteries, experimental research is essential for identifying and testing appropriate materials

and for establishing design and manufacturing requirements for adequate reliability and safety. Laboratory-scale testing is needed to verify performance of cell prototypes before moving on to scaled-up production. Experimental results are also needed to validate theoretical and computational models and to ensure the legitimacy of the analyses performed using such models. The importance of experimental work cannot be understated, and ongoing efforts in a vast number of research directions continue to provide valuable breakthroughs in battery science.

Nonetheless, the design and optimization aspects of engineering have become increasingly reliant on computational modeling and simulation tools to advance technology beyond the scope of experimental approaches. This is especially true for complex systems and technologies with a large number of design considerations and design variables, and lithium-ion batteries are no exception. Computational models offer several key advantages for studying such complex systems: eliminating the need for special laboratory equipment, the ability to quickly obtain data from a large number of cases in parallel, and the ability to precisely control all parameters to reduce uncertainty. Given the importance of developing and utilizing accurate models for lithium-ion battery behavior and performance, this section presents an overview of past and current modeling efforts.

## 4.1 Strategies and approaches for battery modeling

Many types of models have been developed to study a wide variety of problems related to lithium-ion battery components and systems. The choice of model strongly depends on the nature of the problem of interest, and in general the following must be defined:

1. The system or component to be modeled (can range from individual components within a battery cell, to individual cells, to complex systems, such as vehicles in which the battery is one component);
2. The level of detail into the physical processes that needs to be achieved (the selection of governing equations, and the geometric or morphological representation of the battery system and its components); and
3. The computational expense that can be afforded for the analysis (the required number of simulations, as well as the cost of each simulation).

Owing to the range of scenarios that must be considered in different problems, battery models vary considerably in structure and complexity. However, certain classes of models and techniques have proven to be especially useful and have motivated a large number of notable developments. The computational complexity and level of detail of several of these classes of models are illustrated in Figure 4.

The simplest battery models to be widely used are equivalent circuit models, which represent the entire battery by the equivalent characteristic behavior (most commonly resistance and capacitance) that it would have as part of a circuit (Liaw *et al.*, 2004). Equivalent circuit models are lumped-parameter models, with parameters estimated from empirical measurements, and do not model the internal states of the battery. Despite their simplicity, circuit models can provide relatively accurate steady-state and transient behavior of lithium-ion systems, and hence are useful for the analysis and control of larger systems containing batteries, when only a rough approximation of system-level battery performance is needed (Hu, Li, and Peng, 2012).

For more sophisticated applications, equivalent circuit models may not contain sufficient detail to be useful. For example, it is often important to be able to resolve the distribution of lithium concentration and electric potential within a battery cell. In such cases, a lumped-parameter approach is inadequate, and a model containing physics-based equations is necessary. A notable example of a model capable of simulating the distribution of ion concentration and potential within individual cells is the homogeneous pseudo-2D porous electrode model (Doyle, Fuller, and Newman, 1993), sometimes referred to by the name of the corresponding Fortran program, *dualfoil*. This model has the advantages that it has been experimentally validated (Doyle *et al.*, 1996) and that it is computationally fast while providing a level of detail that models the most relevant physics within battery cells. These advantages make this model suitable for analyzing a variety of battery problems, such as solid-state diffusion (Smith and Wang, 2006) and electrode design (Yu *et al.*, 2012).

Although 1-D and pseudo-2D models based on homogenization offer a good balance of computational efficiency and physical detail for many problems, in many other cases, either a more detailed treatment of important physical phenomena or improved computational speed is needed. Various reduced-order modeling techniques have been applied to improve the computational speed of simulations, including model reformulation (Subramanian *et al.*, 2009), proper orthogonal decomposition (Cai and White, 2009), and surrogate modeling (Du *et al.*, 2010; Shyy *et al.*, 2011), among others. Such improvements in computational speed are needed for control systems where little computational time is allowed at each iteration (Perkins *et al.*, 2012; Randall *et al.*, 2012), or for design optimization problems where many model simulations are required (De *et al.*, 2013; Du *et al.*, 2013a).

Homogeneous models are able to capture the collective effect of certain microstructural parameters by making
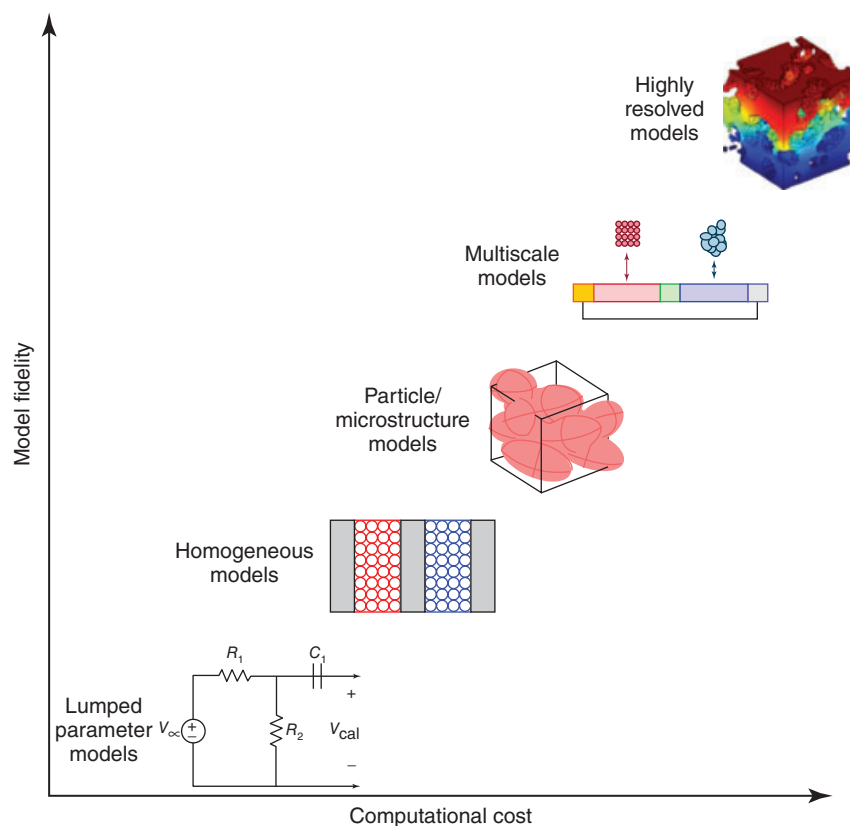
**Figure 4.** Increased accuracy in model comes at the price of higher computational cost.

simplifying approximations based on homogenization. For example, pseudo-2D models calculate rates of diffusion inside idealized spheres to model the effect of particle size. A more accurate treatment can be achieved with more realistic representations of the electrode morphology. Examples of models applying these approaches include those based on both single-particle (Zhang, Popov, and White, 2000; Zhang, Shyy, and Sastry, 2007) and multiparticle (Garcia *et al.*, 2005; Gupta *et al.*, 2011) representations of the microstructure. Single-particle models typically seek to extend homogeneous models by providing a more accurate treatment of localized phenomena, while retaining a fundamental assumption that a single particle is representative of the electrode as a whole. Multiparticle models often relax the homogenization assumption by reconstructing or approximating realistic microstructures composed of particle aggregates to use as a representative volume for the electrode (Zhu *et al.*, 2014).

One limitation of particle-level microstructural or representative-volume models is that they often capture only localized behavior and do not relate local parameter values to macroscopic cell performance. These models can be effective in modeling mechanical stress or heat generation within individual particles, but they are unable to provide any insights into how the distribution of stress or heat may ultimately affect the overall battery. To address this information gap, multiscale models that couple models at different levels of abstraction have been devised. Multiscale modeling methods apply statistical averaging techniques to relate parameters and equations at microscopic spatial or temporal scales (e.g., single or multiple particles) with behavior and performance at macroscopic (cell or electrode) scales. Multiscale methods generally attempt to achieve the fine granularity of microscopic models, while maintaining the computational efficiency of homogeneous models. Examples of specific battery phenomena investigated using multiscale models include intercalation-induced stress in active particles (Golmon, Maute, and Dunn, 2009), mechanical stress and strain on separators (Xiao, Wu, and Huang, 2010), and thermal-electrochemical coupling (Lee *et al.*, 2013). A schematic representation of a typical multiscale battery cell model is shown in Figure 5. Note that while models with two length scales are the most popular, it is possible to include more.

Finally, highly resolved models have long been envisioned as a way to simulate entire cells and batteries with a high
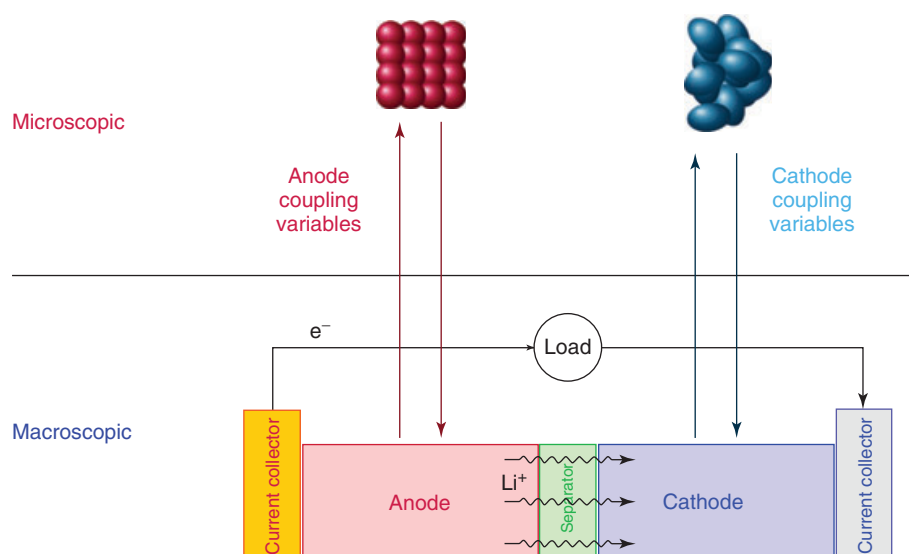
**Figure 5.** Representative multiscale cell model with two length scales.

level of detail. In many fields, this is referred to as brute-force simulation or direct numerical simulation, as there is no attempt to simplify the model using the techniques discussed earlier. Unfortunately, high resolution simulations for entire batteries are currently not practical because of the enormous computational expense that would be required to model the whole system at the molecular level. However, highly resolved 3-D models for small representative cross sections have been developed (Wang and Sastry, 2007), as well as 3-D cell and pack models with limited spatial resolution (Jeon and Baek, 2011).

## 4.2 Recent progress in modeling development

As evidenced in the preceding section, much progress has been made in recent years in the development of modeling capabilities for analyzing and designing lithium-ion batteries. Nonetheless, limitations in existing models continue to motivate numerous ongoing developments. Current efforts include both the extension of existing modeling approaches, and the formulation of novel methodologies to meet the needs of increasingly complex problems aimed at improving the understanding and design of lithium-ion batteries.

An example of building on existing models is the incorporation of physics-based battery models into system-level modeling architectures (Ramadesigan *et al.*, 2012) and battery management systems (Prada *et al.*, 2012; Lu *et al.*, 2013), where traditionally, more simplified approaches such as equivalent circuit models have been used. Other examples can be found in the domain of multiscale modeling, with models gaining increasing complexity via the integration of multiple existing models, such as combining microstructural models for electrochemical kinetics at particle interfaces with homogeneous cell models (Du *et al.*, 2014).

Notable research directions among novel modeling developments include modeling capacity fade and other aging phenomena, atomistic and molecular approaches, and state estimation techniques for battery prognostic and diagnostic purposes. As will be discussed later in this article, the modeling of battery degradation has historically attracted considerable interest. However, progress on this topic has proceeded relatively slowly compared to other areas of battery science, although researchers such as Ramadass *et al.* (2004) and Liaw *et al.* (2005) have made important developments. This is due to both the complexity of the mechanisms (and the corresponding difficulty of developing theoretical models) and the lack of empirical data needed to validate such models. However, with the advent of EVs and the large amount of cycle life data obtained from the associated testing, the evident need for better degradation models has motivated numerous new developments. Recent novel battery degradation models include those of Lin *et al.* (2013), Fu *et al.* (2014), Xie, Li, and Yuan (2014), and Kang, Conlisk, and Rizzoni (2014).

In contrast to the microstructural models described in the preceding section, which use a continuum representation of the finest scale at which battery materials are analyzed, it is possible to model materials at the atomic and molecular scale instead. Such atomistic and molecular dynamics (MD) simulations have been developed to investigate, for example, how quantum effects can affect macroscopic properties of materials. These modeling approaches are motivated by inconsistencies in experimental results stemming from differences

in measurement techniques and operating conditions that make models difficult to validate. For instance, Park *et al.* (2010) have found that reported values for parameters such as diffusivity and conductivity can vary by several orders of magnitude depending on the measurement technique, even for the same material. As an alternative to relying on experimental values of material properties and other parameters, atomistic and MD simulations can be applied to calculate these quantities from first principles using statistical averaging techniques. A few examples of properties that have been investigated using these approaches include lithium transport (Islam *et al.*, 2005), diffusion-stress-concentration relationships (Haftbaradaran *et al.*, 2011), and traction and separation at interfaces (Lee *et al.*, 2014).

Another important area of active research in which EVs have been a critical driving force is in state estimation and control for onboard batteries. It is important to be able to monitor important parameters such as SOC and state of health with low computational cost. This information is needed so that control strategies can be implemented to optimally distribute the load to the various cells within a large battery pack to maximize efficiency and minimize losses. State of health is an especially important quantity to estimate for reliability and safety reasons. Motivated by the need for more accurate prognostic capabilities, many recent developments have been made for estimating state of health, using techniques such as neural networks and Kalman filtering (Andre *et al.*, 2013), genetic algorithms (Chen *et al.*, 2013), and support vector regression (Weng *et al.*, 2013).

## 5  BATTERY DESIGN

While the intrinsic material properties determine the theoretical maximum performance of lithium-ion batteries, cell design is essential for minimizing the gap between achievable energy densities and the corresponding theoretical limits. In addition, different electrode materials have different properties such as particle size, conductivity, and diffusivity. It is essential that such variations in properties be considered in the cell design process. With the experience and knowledge gained from decades of experimental and simulation studies on batteries, battery researchers have been able to maximize the energy density of an electrochemical system by minimizing the amount of nonenergy contributing mass such as electrolyte and various additives. A lithium-ion cell can be represented using the diagram shown in Figure 6, where the porous electrode is represented as a mixture of spherical solid particles and liquid electrolyte. The solid phase is governed mainly by diffusion requirements, as charges stored in the center of the particles can only undergo electrochemical reaction upon reaching the surface. In
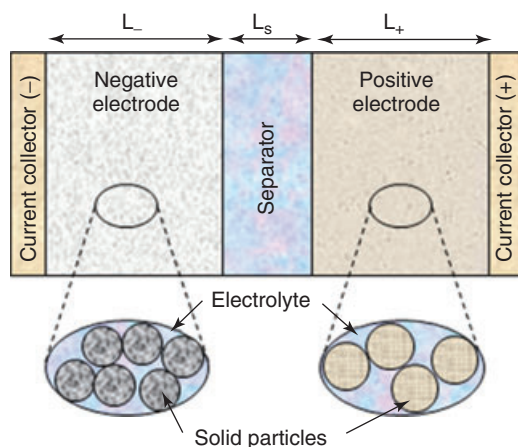


**Figure 6.** Schematic diagram of a lithium-ion cell representing a simplified homogeneous and porous electrode.

the liquid phase, the transport equation is governed by diffusion due to the concentration gradient of ionic species and the migration due to electric potential gradients. While it is desirable to maximize the ratio of charge-storing active material by minimizing the electrode porosity and increasing electrode thickness, it is important to ensure adequate rate of transport by ensuring adequate amount of electrolyte to minimize gradient-induced resistance and to prevent under-utilization of active materials under high discharge rate.

Numerous researchers have optimized the morphological design of electrodes using physics-based electrochemical models. Newman (1995) optimized the geometric design of a cell with respect to the positive electrode thickness and porosity using a simplified reaction zone model. By confining the lithium-ion intercalation to a narrow zone in the positive electrode, he obtained an analytical solution and related the dependence of energy capacity to parameters such as electrode thickness and OCV. Du *et al.* (2013b) expanded on the nondimensional analysis of the cell performance by optimizing the energy density with respect to cycling rate, particle size, diffusivity, and conductivity using a surrogate modeling formulation. The cell performance was quantified using nondimensional diffusivity and conductivity parameters, and in each case, a threshold value is determined as the limiting factor in cell performance. More involved optimization efforts attempt to optimize the spatial distribution of porosity and particle size within the electrode (Ramadesigan *et al.*, 2010; Golmon, Maute, and Dunn, 2012). Although current cell fabrication techniques are unable to allow such a fine degree of control over the internal morphology of the electrode, microstructural electrode design may be possible in the future with better understanding of the physical processes and advanced nanoscale fabrication techniques.
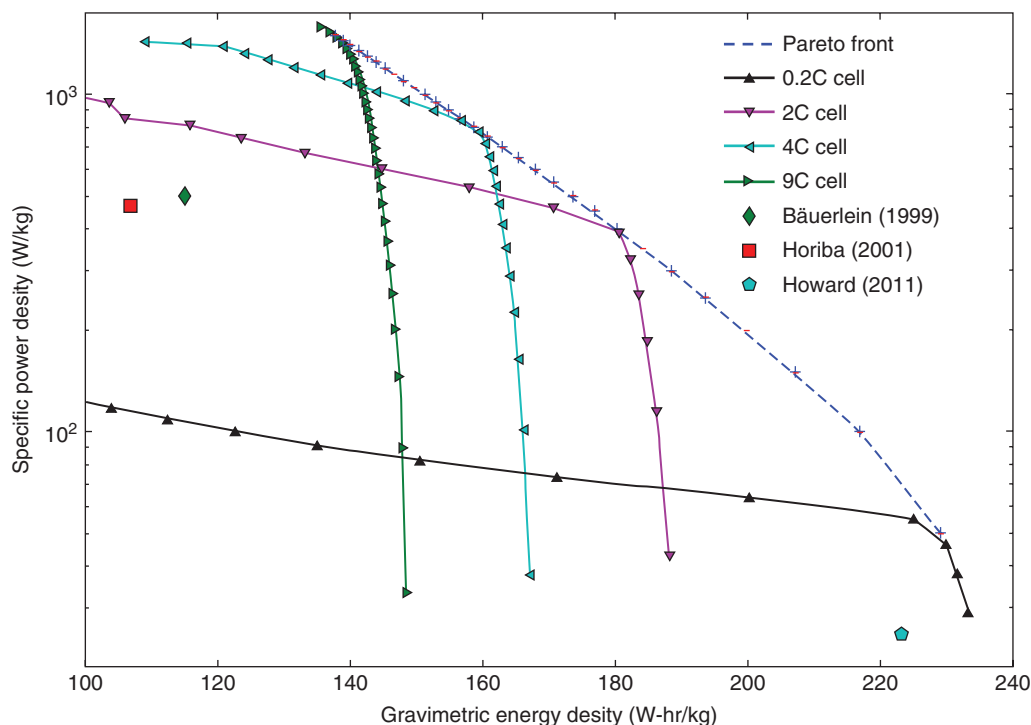
**Figure 7.** Comparison of optimal Pareto front of cell designs with Ragone plots of optimal cells. *Source*: From Xue *et al.*, 2013. Reproduced by permission of ECS – The Electochemical Society.

Given that the need for increasing active material packing is at odds with high transport rate, the energy density and the power density are two competing objectives that have to be balanced for the specific discharge requirement of a cell. A cell with a thick electrode and low porosity is designed for high energy density, whereas a cell with a thin electrode and high porosity is designed for high power. Figure 7 illustrates the importance of having a properly designed cell for different cell requirements by comparing the Ragone plot with the Pareto front of the optimally designed cells (Xue *et al.*, 2013). While high power cells are able to meet large power requirement, they do not provide much additional energy capacity at low discharge rate. Conversely, have maximum energy density at low power requirement. However, they are unable to meet power requirements that significantly exceed their design points.

The optimal cell design balances the two competing objectives of energy and power by varying the electrode thickness and porosity with cell requirements, as shown in Figure 8. As the cell power requirement increases, the porosity increases, while the electrode thickness decreases to ensure that the cell capacity is fully utilized. While the need to increase porosity and decrease electrode thickness is clearly understood, the mathematical relationship between the two parameters can be quantified by performing a

sequence of numerical optimizations for different sets of cell requirements. In this case, the optimal variations of electrode thickness and porosity—such as those shown in Figure 8—are dependent on the Coulombic capacity of the active materials, resulting in a charge ratio of exact unity between the two electrodes and a constant active material mass ratio (Xue *et al.*, 2013).

For an ideal cell without any degradation or material imperfections, it would be easy to obtain the optimal cell design, as properties such as particle size, solid phase conductivity, and diffusivity all converge to their respective limits. However, practical cell design considerations include additional details such as degradation mechanisms, safety concerns, capacity preservation over repeated cycling, and temperature stability. Such factors create additional challenges and cause cell designs to deviate from theoretically optimal values in order to address practical concerns. For instance, safety concerns impose a minimum thickness on the separator. However, this minimum thickness constraint comes at the price of additional parasitic mass and reduced ionic conductivity in the electrolyte. In addition, concerns regarding overcharge leading to lithium plating on the anode require the cathode charge capacity to be less than that of the anode. Finally, pack-level considerations impose additional constraints on the design and operation of individual cells,
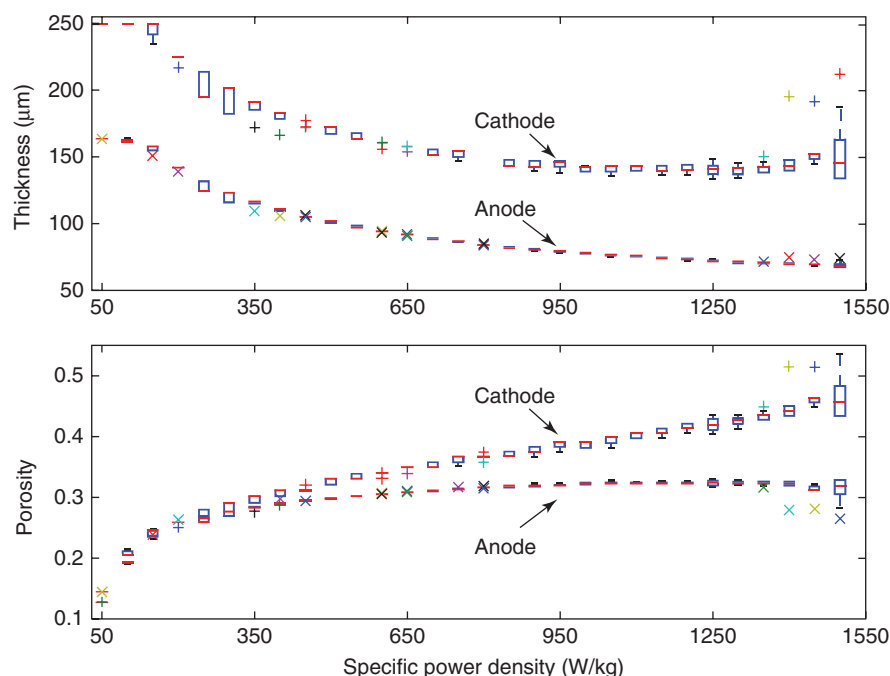
**Figure 8.** Optimal electrode thickness and porosity variations with power requirement. *Source*: From Xue *et al.,* 2013. Reproduced by permission of ECS – The Electochemical Society.

although recent progress has been made in bridging the gap between cell design and pack design (Xue *et al.*, 2014). The following section offers an overview of the critical challenges in the development of the next generation of batteries.

# 6    ISSUES AND CHALLENGES

## 6.1    Cell degradation

Throughout their operational life, batteries experience degradation in capacity and internal mobility owing to a variety of irreversible mechanisms resulting from charge and discharge cycles. Although recent innovations in technology and design have allowed HEVs and PHEVs to achieve competitive performance metrics, the limited cycle life of the onboard battery has important implications on the cost competitiveness of such vehicles. This is in large part due to the high cost of replacing a large lithium-ion battery pack, and the effect this has on the warranties offered by automobile manufacturers. Declining prices with the maturation of the technology can help mitigate this concern, but considerable investment has nonetheless been made toward understanding the degradation of lithium-ion batteries and improving their cycle life.

One of the key challenges in lithium-ion applications is degradation modeling to account for and predict capacity

and power fade. Cell degradation is difficult to model, as it cannot be accounted for by any single process. Instead, degradation is the result of the coupling and interaction of a number of processes. In addition, different electrode materials, additives, and chemical compositions often result in completely different degradation mechanisms. Various models have been proposed to simulate cell breakdown owing to prolonged cycling. Physics-based models require additional governing equations for side reactions and parameters to account for species and impedance terms. Obtaining validated equations and parameters has proven to be extremely difficult and time-consuming, as all relevant degradation mechanisms and their interactions have to be included. A simpler approach is to build an empirical model based on cell cycling data from which cell performance can be extrapolated. As an example, an equivalent circuit model can be coupled with empirical functions to model internal resistance rise and capacity loss (Liaw *et al.*, 2005). Fatigue models, which model structural failure from accumulated stress due to repeated cycling, can also be used to predict cell degradations (Onori *et al.*, 2012). However, a limitation of these types of models is that a large quantity of experimental data is needed and that the models are battery-specific.

In the simplest terms, cell breakdown can be differentiated into two types: capacity fade, which is the loss of cyclable lithium or active materials in electrode that results in lower cell capacity, and power fade, which is the loss of power

**Table 3.** Common causes and effects of lithium-ion degradation.

| Component | Causes | Effects |
|---|---|---|
| Anode | Electrolyte decomposition causing SEI growth | Loss of lithium |
| | | Impedance rise |
| | Contact loss of active materials | Loss of intercalation sites for lithium |
| | Particle fraction due to volume change during cycling | Loss of active materials |
| | | Loss of lithium |
| Cathode | Active material dissolution | Loss of intercalation sites for lithium |
| | Phase transition | Loss of intercalation sites for lithium |
| | | Impedance rise |
| | Solvent co-intercalation | Gas evolution |
| | | Loss of active materials |
| Others | Current collector corrosion | Impedance rise |
| | | Uneven distribution of current and potential, causing overpotentials |
| | Binder decomposition | Loss of mechanical stability |
| | | Loss of lithium |
| | Conductive agent oxidation | Impedance rise |

capability due to increase in cell impedance (Vetter *et al.*, 2005). Attempts have been made to study the various degradation mechanisms by their causes and effects and how they affect different cell components. Table 3 summarizes the most critical degradation processes.

The anodes in most commercially available lithium-ion batteries are made of carbonaceous materials, especially graphite. Various aging mechanisms in graphite-based cells have been studied extensively (Arora, White, and Doyle, 1998; Broussely *et al.*, 2005). The main degradation mechanism has been identified as solid-electrolyte interface (SEI) growth, which forms a passivating layer on the anode surface. While SEI growth causes both a loss of lithium and a rise in impedance, the caveat is that the SEI also protects the anode from further attack by electrolyte, and thus provides a stabilizing effect on the anode after the initial formation cycles to reduce the amount of cyclable lithium lost thereafter. However, the SEI layer continues to grow, leading to increased impedance and the eventual inability of the cell to meet its power requirements.

Cathodes, on the other hand, have different material choices, and the degradation mechanisms are very much material dependent. Manganese oxide undergoes structural change, dissolution of active material, and electrolyte oxidation (Park *et al.*, 2011); cobalt oxide dissolution prevents utilization of the full intercalation range; whereas surface effects due to passivation cause power loss in mixed nickel cobalt oxide cathodes.

Some of the processes highlighted here can have secondary effects that lead to further degradation. For instance, SEI growth results in a reduced interfacial surface area between the electrolyte and the solid particles, and volume fraction change during intercalation causes porosity changes, both of which lead to further impedance rise and power fade (Li *et al.*, 2001). Loss of active materials in

the electrodes results in imbalance in capacity, causing overcharge or discharge, which leads to further degradation.

The degradation processes are also temperature dependent. At low temperature, ion intercalation rate into carbon is reduced, leading to metallic lithium plating and dendrite growth during charging, which could result in internal short circuit and catastrophic cell failure (Smart *et al.*, 1999). High temperature, on the other hand, causes increased rate of electrolyte degradation, causing increased thickening of the SEI layer and further loss of cyclable lithium (Ramadass *et al.*, 2004).

From a design perspective, numerous approaches are taken to prolong cell life. As cyclable lithium is irreversibly consumed during the initial cycles to form the protective SEI layer, it is important to choose the electrode capacity ratio accordingly to account for the loss of lithium and to prevent subsequent overcharge during cycling. This is often achieved by constraining the capacity ratio of the two electrodes. In addition, the need for high interfacial surface area for fast kinetics has to be balanced against the high rate of electrode dissolution. Therefore, the particle sizes should be chosen based on the discharge rate requirement.

Various additives can be used to improve life cycle of lithium-ion batteries. Additives can be added to the electrolyte to: (i) stabilize the SEI layer, (ii) reduce lithium consumption and gas generation during SEI formation, (iii) form a protective coating on the cathode, (iv) improve thermal stability of lithium salt, (v) improve physical properties of the electrolyte, and (vi) improve cell safety (Zhang, 2006). Some of the more common additives include vinylene carbonate (VC), vinyl ethylene carbonate (VEC), and lithium bis(oxalato) borate (LiBOB). For silicon-based anodes, fluoroethylene carbonate (FEC) has been shown to improve cell cycle life.

Issues related to calendar life, which is caused by factors beyond cycling, need to be addressed as well. While degradation due to cycling can be minimized by limiting DOD and using protection circuitry, improvements in calendar life also need to account for mechanisms that occur when the battery is not being cycled. Such considerations include the design of the battery pack configuration, the selection of electrode materials within individual cells (e.g., to minimize self-discharging behavior), and environmental conditions (e.g., the protective casing and thermal regulation systems). Calendar life is highly correlated with storage temperature (Zheng, Gozdz, and Amatucci, 1999), as it causes the decomposition of $LiPF_6$ into $LiF$ and the highly reactive $PF_5$, which subsequently causes electrode dissolution.

## 6.2    Fast charging

In addition to limited range and unproven cycle and calendar life, fast charging is highly desirable to widen the acceptance of EVs and their battery technology. While only a few minutes are needed to fill a tank of gasoline or diesel fuel in a conventional vehicle that provides hundreds of kilometers of range, an EV with much shorter range still requires several hours to fully charge. The problem of fast charging even has relevance in more established technologies such as smart phones, in which expansions in functionality demand ever larger batteries. Despite considerable research effort into fast-charge technologies, their implementation has not been realized in real-world applications, and slow-charging rates remain a notable inconvenience. Promising research directions to address this issue include the development of novel materials suitable for fast-charge batteries (Zaghib *et al.*, 2011), and of optimal charging strategies (Kristoffersen, Capion, and Meibom, 2011). Infrastructure costs need to be addressed as well, as extremely high current or voltage is needed to enable fast charging, and this requirement is beyond what current electrical grid technologies can handle. Overcoming the problem of charging rates will most likely require continued advances in all these areas.

## 6.3    Safety

Safety is an essential design consideration that must be adequately satisfied for all engineering systems and technologies. A recent example of the importance of safety is the replacement of nickel-cadmium (Ni-Cd) batteries with nickel metal-hydride (Ni-MH) equivalents, largely motivated by their superior safety characteristics when charging. Safety is an especially important concern for lithium-ion batteries, as they are being installed in high risk applications such as EVs and aircraft, where failure

can have severe consequences. A notable example is the Boeing 787 Dreamliner, a long-range jet airliner designed to significantly improve fuel efficiency compared to older aircraft using lightweight structures and increased electrification. The 787 is able to reduce fuel consumption during idling and taxiing by replacing mechanical systems with more efficient electrical ones. However, this dependence on electrical systems places a greater demand on the batteries and generators to supply sufficient electricity. The hidden costs of this dependency were revealed in 2013, when the entire fleet was grounded because of safety and reliability concerns over leaking in the 787s battery packs (Williard *et al.*, 2013). This high profile incident serves as a reminder that although lithium-ion batteries have become a mature technology, improvements in reliability are still needed.

The problem in improving the safety of lithium-ion batteries is compounded by the complex mechanisms that can initiate battery failure. Catastrophic failure involving fires and explosions is commonly caused by thermal runaway, which can be triggered by a variety of factors, including electrochemical reactions and microstructural decomposition in either electrode (Wang *et al.*, 2012). Although thermal runaway can be avoided by carefully selecting the battery materials (Mandal *et al.*, 2006), it is by no means the only phenomenon that can be responsible for safety problems in batteries. Battery packs in EVs can be subject to large mechanical loads that can permanently degrade the cells and damage the protective packaging around the pack. Similar problems can also be caused by uneven thermal expansion due to variations in the ambient temperature around the battery. Finally, the insertion and extraction of ions into and out of the active electrode materials also causes stress and strain, increasing the risk of short-circuiting and long-term damage to the cells (Zhang, Shyy, and Sastry, 2007).

The challenge of building better batteries is not limited to avoiding these safety issues. The more pertinent problem is that the obvious solutions to these problems often contradict other design considerations. For example, thicker casings in EV battery packs can provide superior protection against mechanical stress, but increase the weight of the pack and ultimately hinder the performance of the vehicle. The true challenge is to establish methods for designing batteries that optimally balance performance, safety, and other requirements.

## 7    THE FUTURE

Lithium cobalt oxide was used in the first commercial lithium-ion battery, and after 20 years, it is still used in today's lithium-ion batteries because of its high capacity.

Numerous positive electrode materials have been proposed and commercialized since. However, none of them has been shown to be significantly better in terms of energy density. Some materials such as manganese chromium oxide have higher capacity than lithium cobalt oxide, but material toxicity and costs have restricted their adoption. Compared to the progress in semiconductors that follow Moore's Law, the increase in energy density of batteries has been much slower.

High fidelity numerical models that utilize high performance parallel computing have been instrumental in accelerating the progress of many other fields, but their adoption in battery research has been slow. This is due to the inherent difficulty in battery modeling, as it is a multidomain, multiscale, and multidisciplinary problem. It is only recently that researchers have begun using complex models to study reactions at the atomic or molecular level. The goal is to understand how macroscopic properties can be derived from quantum first principles, and to then apply this knowledge to enable microscopic tailoring of cell materials. Computer algorithms are also used to screen for compounds as potential electrode materials. For example, the Materials Project combines supercomputing with the latest electronic structure models to create a comprehensive database of properties of materials (Ceder and Persson, 2013). To date, the database contains more than 49,000 compounds, of which approximately 1400 can be used as lithium intercalation electrodes.

Numerous electrode materials and cell chemistries have been proposed as alternatives to the current generation of Li-ion batteries. Some of the potential battery technologies have been highlighted in Table 4. In addition, batteries using fluoride as anionic shuttles or alkali earth metals as multivalent intercalation materials have been proposed as well. They offer interesting low cost alternatives to lithium-ion chemistry. However, it is too early to tell if such efforts will prove to be ultimately successful.

Among the next generation of lithium-based battery technologies currently under development, technologies such as Li-metal, silicon anode, lithium-sulfur, and lithium-oxygen batteries have been identified. While these technologies theoretically offer significant improvements over current

**Table 4.** Performance comparison of various future cathode systems.

| Battery Type | Voltage (V) | Theoretical Capacity (mAh/g) | Theoretical Specific Energy (Wh/kg) |
|---|---|---|---|
| Conventional Li-ion | 3.8 | 155 | 387 |
| Li-sulfur | 2.2 | 1600 | 2600 |
| Li-air (nonaqueous) | 3.0 | 3800 | 11,000 |
| Al-air | 2.7 | 3000 | 8100 |
| Zn-air | 1.65 | 820 | 1086 |

lithium-ion batteries, in practice, their development has been hindered by issues related to long-term stability.

A lithium-metal battery has lithium metal foil as the anode, which is consumed in the electrochemical reaction. Lithium metal has obvious advantages (low weight and high cell potential), and is commonly used in primary lithium batteries. However, cycle life tends to be poor owing to uneven dendrite growth during charge cycles, when the previously consumed lithium metal is restored to the anode. This leads to significant safety and reliability problems owing to short-circuiting of the cell (Howlett, MacFarlane, and Hollenkamp, 2004). Given its obvious energy density advantages, efforts have been made to address the dendrite growth problem (Scrosati and Garche, 2010). Most recently, dendrite growth suppression has been achieved using a separator with shear modulus much greater than that of lithium (Ferrese and Newman, 2014).

Alternatively, silicon has emerged as a viable replacement for carbon-based insertion materials. Silicon has problems of its own as well, such as excessive volume expansion, leading to unstable electrolyte interphase growth on the silicon surface (Aurbach, 2000; Kasavajjula, Wang, and Appleby, 2007). There has been recent progress by immersing silicon-based anode in a conducting polymer hydrogel (Wu et al., 2013), thereby creating a 3-D network that provides porous volume for expansion, as well as a continuous electrically conductive network.

Sulfur has been identified as a potential cathode material as it has the possibility of providing a tenfold increase in energy density over current lithium-ion batteries. Moreover, sulfur is an element that is naturally abundant, nontoxic, and inexpensive to obtain (Wang et al., 2008; Jeon, Yeon, and Chung, 2003). However, development of sulfur-based cathodes has been plagued by low active material utilization, poor cycling, and low Coulombic efficiency (Mikhaylik and Akridge, 2004).

Lithium-air batteries, which couple a lithium anode with an air cathode, have extremely high theoretical energy capacity (11 kWh/kg) that is comparable to that of gasoline. The first lithium-air battery was proposed in 1996 (Abraham and Jiang, 1996). However, a desirable rechargeable behavior has not been achieved because of poor power output and a limited operating temperature range. To achieve the desired performance for a Li-air battery, designers need to master both the lithium and oxygen electrodes and overcome a multitude of scientific and technical challenges (Girishkumar et al., 2010). Practical constraints on Li-air batteries, such as the requirement for an air filter, reduce the energy density of such a battery system to approximately 400 Wh/kg, significantly below the theoretical limit.

Finally, alternative battery materials have been examined because of environmental considerations. A key motivation

behind HEVs and EVs is their reduced energy consumption and environmental impact compared to conventional vehicles. However, current manufacturing processes are energy intensive for large battery packs, resulting in vehicles with a high environmental manufacturing cost. In addition, the recycling process for lithium-ion batteries is not well established because of the high cost of the process. Lithium-ion batteries based on organic materials have shown promise in this regard owing to their recyclability and renewability (Tarascon and Armand, 2001). Although they generally demonstrate reduced energy and power performance and exhibit limited cyclability, they remain a viable low environmental impact alternative in moderate-performance applications.

# 8    CONCLUSION

Steady gains in energy and power density have enabled the development of many high performance applications using lithium-ion batteries, such as multifunctional portable electronic devices and HEVs. Efforts in experimental and numerical modeling have provided researchers with a better understanding of the physical processes occurring in the cell, enabling better cell designs with greater energy capacity and long cycle life. However, lithium-ion batteries still suffer from numerous limitations, and considerable research is currently focused on overcoming these. Apart from continued efforts to improve energy and power density (through higher voltage, higher capacity, and lower weight materials), critical active research areas of improvement include extending cycle and calendar life, enabling fast charging for high performance applications, improving safety, and reducing environmental impact. Researchers have also begun to look beyond conventional lithium-ion cells for the next major breakthrough in energy density. Promising developments in silicon-based anodes, lithium-sulfur and lithium-air batteries have been made, although it could be up to a decade before one of these new technologies become commercially viable. Despite the drawbacks and low energy density compared to fossil fuel, lithium-ion batteries still offer the best solution to achieve energy independence, reduce carbon footprint, and achieve sustainable development.

# RELATED ARTICLES

Rechargeable Battery Energy Storage System Design
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