Materials and Processing for Lithium-Ion Batteries

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Lithium-ion battery technology is projected to be the leapfrog technology for the electrification of the drive-train and to provide stationary storage solutions to enable the effective use of renewable energy sources. The technology is already in use for low-power applications such as consumer electronics and power tools. Extensive research and development has enhanced the technology to a stage where it seems very likely that safe and reliable lithium-ion batteries will soon be on board hybrid electric and electric vehicles and connected to solar cells and windmills. However, the safety of the technology is still a concern, service life is not yet sufficient, and costs are too high. This paper summarizes the state of the art of lithium-ion battery technology for nonexperts. It lists materials and processing for batteries and summarizes the costs associated with them. This paper should foster an overall understanding of materials and processing and the need to overcome the remaining barriers for a successful market introduction.

How would you…

…describe the overall significance of this paper?

Lithium-ion battery technology needs to overcome significant technological, safety, and cost barriers to be successful in the marketplace. Traditionally, battery technology was driven by electrochemical R&D. Today, materials scientists and process engineers can help in overcoming the barriers and understanding failure mechanisms. This paper educates materials scientists and engineers to start that process.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

Lithium-ion battery technology is projected to be the leapfrog technology for the electrification of the drivetrain and to provide stationary storage solutions to enable the effective use of renewable energy sources. However, safety of the technology is still a concern, service life is not yet sufficient, and costs are too high. This paper summarizes the state of the art of lithium-ion battery technology for nonexperts and fosters understanding for materials scientists and process engineers.

…describe this work to a layperson?

Hybrid and all-electric vehicles and renewable wind and solar power rely on efficient energy storage. However, available battery technology needs to overcome significant barriers in cost and efficiency to become reliable and safe enough to work as mobile or stationary storage. Materials scientists and engineers are working to increase their reliability and reduce their cost to become a safe and affordable solution for our energy crisis.

INTRODUCTION

Worldwide battery demand mainly driven by consumer electronics and electric power tools is projected to rise at a 6.9% annual rate through 2010 to $73.6 billion.[1]

The effective use of low-emission and emission-free energy sources, such as renewable—but intermittent—wind and solar energy, demands stationary, high-yield, long-lasting, and low-maintenance electrical energy storage solutions. In 2006, Germany, the leading nation in wind energy utilization as a part of its overall energy production portfolio, wasted 15% of its wind-produced energy due to the lack of suitable electrical energy storage.[2]

Hybrid electric vehicles (HEVs) and all-electric vehicles (EVs) can reduce the U.S. dependence on foreign oil and will contribute to battery demand in the future. Counting engine efficiencies and including electrical energy production, EVs could reduce the use of gasoline to one-fourth of today's consumption and could reduce the U.S. dependence on imported oil to one-sixth of today's level.[3]

The focus of the U.S. Department of Energy's (DOE's) Vehicle Technologies Program is on lithium-ion-based electrochemical energy storage due to the electrochemical potential and theoretical capacity provided by that system. Lithium-ion batteries can provide a reliable rechargeable storage technology. Developments in this program include lithium-ion, lithium-ion-polymer, and lithium-metal technology.

The DOE's short-term goals for power-assist HEVs are met or exceeded in eight of 11 areas, showing the tremendous success of the program. The eight areas include discharge pulse power, regenerative pulse power, available energy, efficiency, cycle life, system weight, system volume, and self discharge. Still, three goals seem to be more challenging and remain unmet: operating temperature from –30°C to 52°C, a lifetime of 15 years, and a selling price below $500 to $800 per system at 100,000 units produced per year.[4] For plug-in hybrid electric vehicles (PHEVs) in the intermediate term

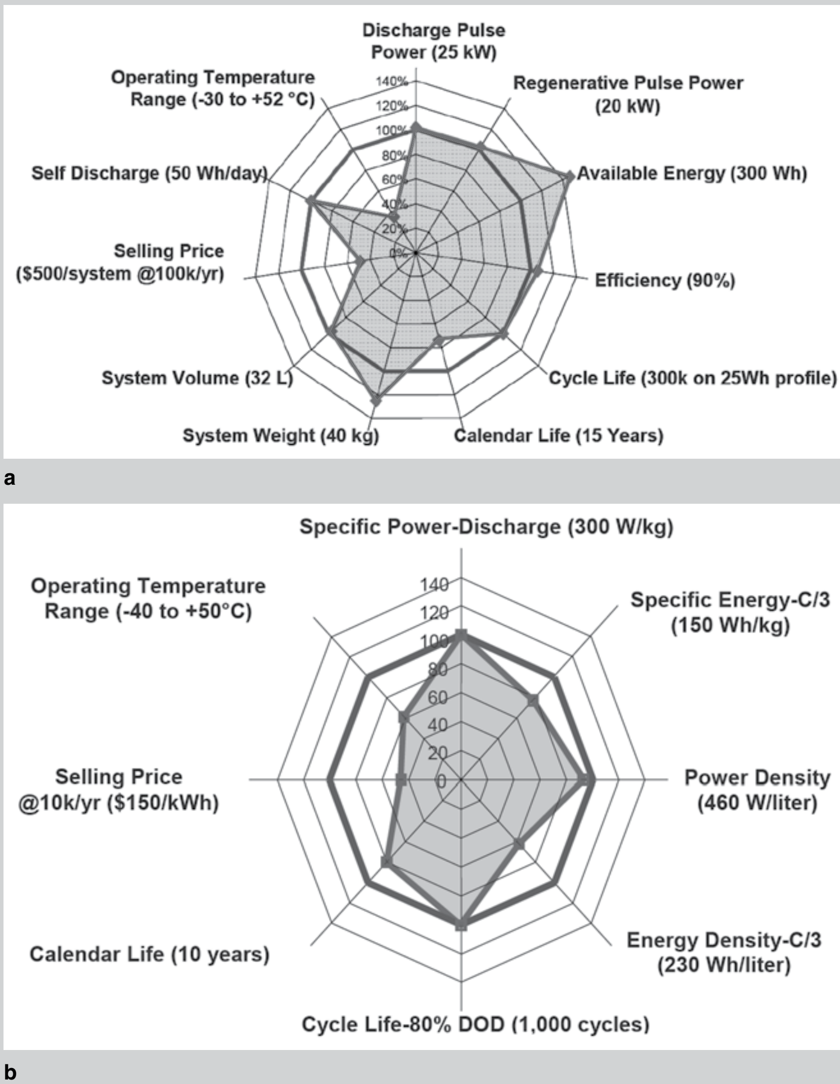


Figure 1. A battery technology spider chart for: (a) HEVs and (b) EVs. The 100% line equals the DOE target for HEVs and USABC target for EVs; the gray area and line represent technological achievements.[4,5]

and for EVs in the long term, accomplishments are far from meeting the goals, and significant material and processing technological barriers need to be overcome. Figure 1 illustrates the DOE and U.S. Advanced Battery Consortium (USABC) goals and milestones met for HEV and EV applications.

The DOE program is focused on overcoming the technical barriers associated with HEV battery technology, namely cost, performance, safety, and life:[6]

- Cost—Current lithium-ion-based battery cost per kilowatt is approximately a factor of 2 too high. The main costs are associated with the high cost of raw materials and materials processing as well as the costs of the cell, packaging, and manufacturing.
- Performance—Performance barriers are mostly related to reduced discharge power at low temperature and loss of power due to use and aging.
- Safety—Actual lithium-ion battery technology is not intrinsically safe. Short circuit, overcharge, over-discharge, crush, and high temperature can lead to thermal runaway, fire, and explosion.
- Life—Hybrid engine systems have an estimated 15 year lifetime. Battery technology needs to meet this target with a goal of 300,000 charging cycles. The cycle life has been demonstrated but the calendar life has not.

Historically, electrochemistry and device engineering have dominated the development of batteries. The above-mentioned performance barriers are materials-related problems. Poor low-temperature performance is a diffusion problem at low temperature. Loss of power due to use is mostly a problem related to mechanical behavior, crack initiation and growth followed by fatal fracture, and subsequent coating and passivation of surfaces. Additionally, materials development and materials-processing development need to be addressed in concert in order to reduce cost and create a safe battery technology. Therefore, materials scientists and process engineers are slowly entering the arena in which the goal of reliable, safe, and long-lasting electrical energy storage will be achieved.

BATTERY PRINCIPLE AND BASICS

The smallest working unit in a battery is the electrochemical cell, consisting of a cathode and an anode separated and connected by an electrolyte. The electrolyte conducts ions but is an insulator to electrons. In a charged state, the anode contains a high concentration of intercalated lithium while the cathode is depleted of lithium. During the discharge, a lithium ion leaves the anode and migrates through the electrolyte to the cathode while its associated electron is collected by the current collector to be used to power an electric device (illustrated in Figure 2).

The cell designs and combinations in modules and packs differ greatly. To establish a base understanding, this paper shows the main cell designs and then focuses on materials, processing, and manufacturing with special emphasis on batteries for transportation.

The electrodes in lithium-ion cells are always solid materials. One can distinguish between cell types according to their electrolytes, which may be liquid, gel, or solid-state components. The electrolytes in gel and solid-state cells represent a structural component and do not need additional separators for the effective separation of electrodes and avoidance of short circuits. Cells come in button, cylindrical, and prismatic forms (see Figure 3). A good overview of the cell forms and materials is provided by J. Besenhard et al.[9]

For low-energy and low-power applications, a cell often represents a full battery. For high-energy and high-power applications such as transportation or stationary storage, a number of cells are packaged in a module, and a number of modules are packaged in a battery.

Thin-Film Batteries

A special category is the solid-state thin-film battery. Thin-film batteries consist of only solid materials. The electrolyte is a solid-state ionic glass or crystal, and the components are deposited via vapor deposition techniques. This design offers the highest energy density, safety, and abuse tolerance, but it is only applicable to small devices for special applications and involves the most costly production method. A good review on thin-film battery systems is provided by N.J. Dudney and B.J. Neudecker.[10]

MATERIALS

Cathode Materials

State-of-the-art cathode materials include lithium-metal oxides [such as $LiCoO_2$, $LiMn_2O_4$, and $Li(Ni_xMn_yCo_z)O_2$], vanadium oxides, olivines (such as $LiFePO_4$), and rechargeable lithium oxides.[11,12] Layered oxides containing cobalt and nickel are the most studied materials for lithium-ion batteries. They show a high stability in the high-voltage range but cobalt has limited availability in nature and is toxic, which is a tremendous drawback for mass manufacturing. Manganese offers a low-cost substitution with a high thermal threshold and excellent rate capabilities but limited cycling behavior. Therefore, mixtures of cobalt, nickel, and manganese are often used to combine the best properties and minimize the drawbacks. Vanadium oxides have a large capacity and excellent kinetics. However, due to lithium insertion and extraction, the material tends to become amorphous, which limits the cycling behavior. Olivines are nontoxic and have a moderate capacity with low fade due to cycling, but their conductivity is low. Methods of coating the material have been introduced that make up for the poor conductivity, but it adds some processing costs to the battery.

Anode Materials

Anode materials are lithium, graphite, lithium-alloying materials, intermetallics, or silicon.[11] Lithium seems to be the most straightforward material but shows problems with cycling behavior and dendritic growth, which creates short circuits. Carbonaceous anodes are the most utilized anodic material due to their low cost and availability. However, the theoretical capacity (372 mAh/g) is poor compared with the charge density of lithium (3,862 mAh/g). Some efforts with novel graphite varieties and carbon nanotubes have tried to increase the capacity but have come with the price of high processing costs. Alloy anodes and intermetallic compounds have high capacities but also show a dramatic volume change, resulting in poor cycling behavior. Efforts have been made to overcome the volume change by using nanocrystalline materials and by having the alloy phase (with Al, Bi, Mg, Sb, Sn, Zn, and others) in a nonalloying stabilization matrix (with Co, Cu, Fe, or Ni). Silicon has an extremely high capacity of 4,199 mAh/g, corresponding with a composition of Si_5Li_{22}. However, cycling behavior is poor, and capacity fading not yet understood.

Electrolytes

A safe and long-lasting battery needs a robust electrolyte that can withstand existing voltage and high temperatures and that has a long shelf life while offering a high mobility for lithium ions. Types include liquid, polymer, and solid-state electrolytes.[11] Liquid electrolytes are mostly organic, solvent-based electrolytes containing $LiBC_4O_8$ (LiBOB), $LiPF_6$, $Li[PF_3(C_2F_5)_3]$, or similar. The most important consideration is their flammability; the best-performing solvents have low boiling points and have flash points around 30°C. Therefore, venting or explosion of the cell and subsequently the battery pose a danger. Electrolyte decomposition and highly exothermic side reactions in lithium-ion batteries can create an effect known as "thermal runaway." Thus, selection of an electrolyte often involves a tradeoff between flammability and electrochemical performance.

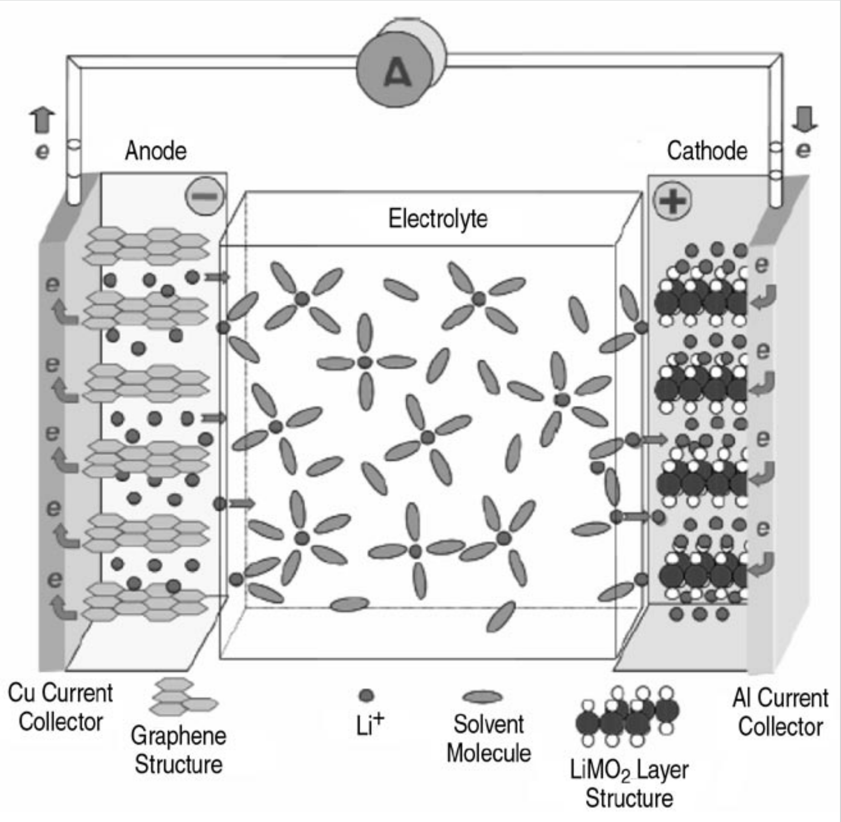
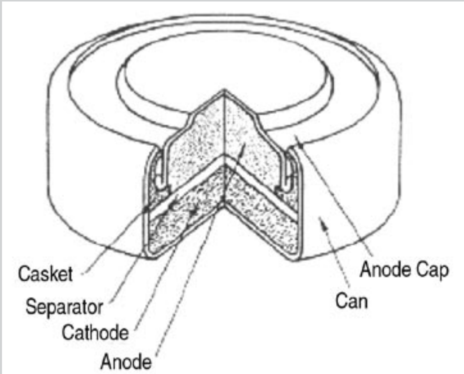


Figure 2. A lithium ion electrochemical cell based on lithium-metal oxide as cathode and graphite as anode (from Reference 7).



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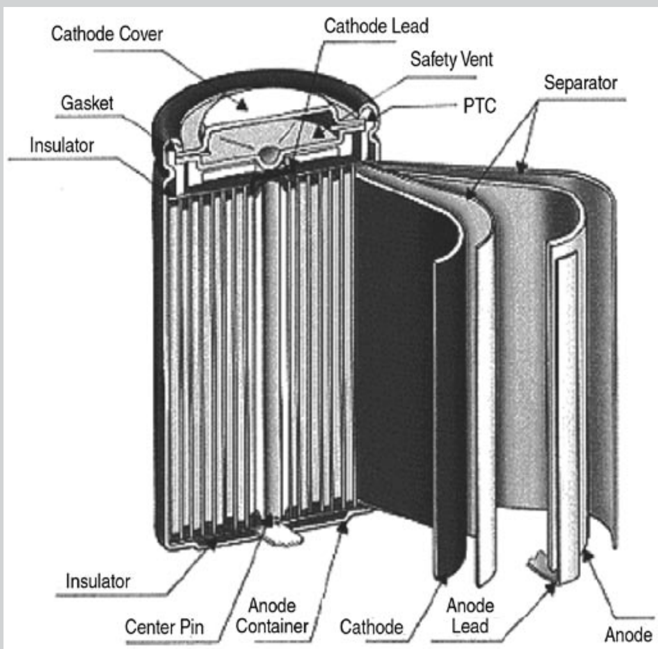

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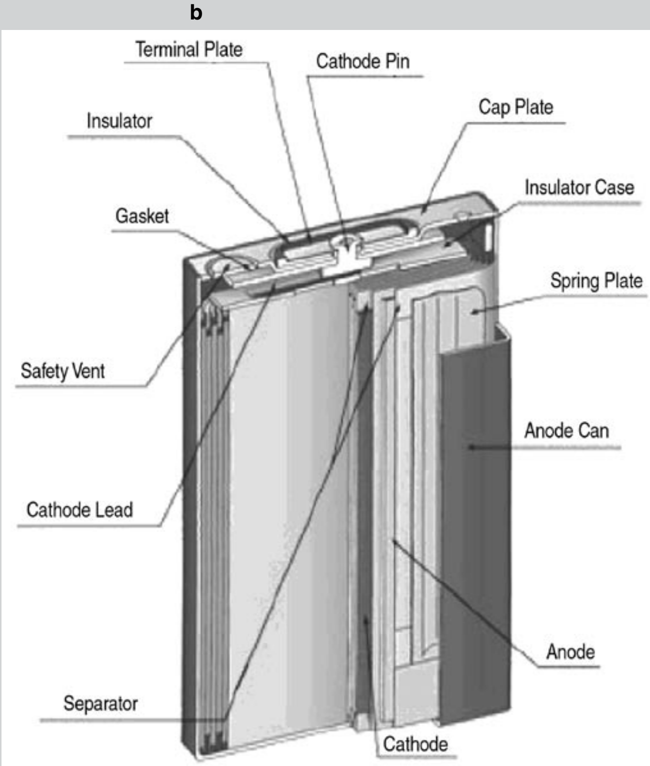

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Figure 3. A schematic of cell forms as found from a multitude of sources:[6–8] (a) button cell, (b) cylindrical cell, and (c) prismatic cell.

Separators have built-in thermal shutdown mechanisms, and additional external sophisticated thermal management systems are added to the modules and battery packs. Ionic liquids are under consideration due to their thermal stability but have major drawbacks, such as lithium dissolution out of the anode.

Polymer electrolytes are ionically conductive polymers. They are often mixed in composites with ceramic nanoparticles, resulting in higher conductivities and resistance to higher voltages. In addition, due to their high viscosity and quasi-solid behavior, polymer electrolytes could inhibit lithium dendrites from growing[13] and could therefore be used with lithium metal anodes.

Solid electrolytes are lithium-ion conductive crystals and ceramic glasses. They show a very poor low-temperature performance because the lithium mobility in the solid is greatly reduced at low temperatures. In addition, solid electrolytes need special deposition conditions and temperature treatments to obtain acceptable behavior, making them extremely expensive in use, although they eliminate the need for separators and the risk of thermal runaway.

Separators

A good review of separator materials and needs is provided by P. Arora and Z. Zhang.[14] As its name suggests, the battery separator separates the two electrodes physically from each other, thus avoiding a short circuit. In the case of a liquid electrolyte, the separator is a foam material that is soaked with the electrolyte and holds it in place. It needs to be an electronic insulator while having minimal electrolyte resistance, maximum mechanical stability, and chemical resistance to degradation in the highly electrochemically active environment. In addition, the separator often has a safety feature, called "thermal shutdown;" at elevated temperatures, it melts or closes its pores to shut down the lithium-ion transport without losing its mechanical stability. Separators are either synthesized in sheets and assembled with the electrodes or deposited onto one electrode in situ. Costwise, the latter is the preferable

Table I. Estimated Materials Content of Typical Lithium-Ion Cells (based on Reference 15)

Material/Component	High-Energy (100 Ah) Cell EV Quantity (g)	High-Energy (100 Ah) Cell EV Part (%)	High-Power (10 Ah) Cell HEV Quantity (g)	High-Power (10 Ah) Cell HEV Part (%)
Anode (dry)				
Active material (graphite)	563.6	16.4	14.1	4.3
Binder	69.7	2.0	3.1	1.0
Current collector (Cu)	151.9	4.4	41.6	12.8
Cathode (dry)				
Active material	1,408.6	41.0	74.4	22.9
Carbon	46.4	1.4	3.2	1.0
Binder	92.9	2.7	6.3	1.9
Current collector (Al)	63.0	1.8	19.4	6.0
Electrolyte	618.0	18.0	44.0	13.5
Separator	60.5	1.8	16.4	5.0
Rest of Cell				
Tabs, end plates, terminal assemblies	66.2	1.9	32.2	9.9
Core	0.9	0.0		
Container	291.0	8.5	70.1	21.6
Total	3,432.7		324.8	

method but poses some other synthesis, handling, and mechanical problems. Solid-state electrolytes and some polymer electrolytes need no separator.

PROCESSING AND MANUFACTURING

Battery discharge is based on the diffusion of lithium ions from the anode to the cathode through the current collector, as shown in Figure 2. This moving mechanism is primarily based on diffusion processes: delivering lithium ions to the surface of the anode, transitioning to and diffusion through the electrolyte, and transitioning to and diffusion into the cathode. Diffusion is the most limiting factor in high-current discharge and charge as well as in low-temperature performance. In addition, the intercalation and deintercalation processes create a volume change in the active electrode materials. This repeated process due to cycling can initiate cracks and can lead to eventual fracture with the result of unusable active electrode material due to disconnection to the current collector or a short circuit and—in case of lithium-metal batteries—a safety hazard due to roughening of the anode and dendritic growth.

Efforts in materials processing and manufacturing to increase performance and to manage unavoidable volume change have been leading toward composite materials with micro- and nano-scaled particles. Nanoparticles can accommodate volume change with minimal risk of crack initiation, and their micro-scaled agglomerates and composites result in minimal diffusion path lengths through the slow diffusion phases (electrodes). A strong focus is on packing density to maximize active material content, open porosity to access the electrolyte, and electronic continuity to guarantee charge exchange to the current collectors.

Cylindrical cells are manufactured and assembled as follows. The electrolytes are formed from pastes of active material powders, binders, solvents, and additives and are fed to coating machines to be spread on current collector foils, such as aluminum for the cathode side and copper for the anode side. Subsequent calendaring for homogeneous thickness and particle size is followed by slitting to the correct width. The components are then stacked to separator-anode-separator-cathode stacks followed by winding to cylindrical cells, insertion in cylindrical cases, and welding of a conducting tab. The cells are then filled with electrolyte. The electrolyte has to wet the separator, soak in, and wet the electrodes. The wetting and soaking process is the slowest step and therefore is the determining factor in the speed of the line. All other needed insulators, seals, and safety devices are then attached and connected. Then, the cells are charged the first time and tested. Often cells have to be vented during the first charge. First charging cycles follow sophisticated protocols to enhance the performance, cycling behavior, and service life of the cells. Recently, efforts have been made in combined and hybrid processing, such as direct deposition of separators onto electrodes and rapid heat treatments.

COST ANALYSIS FOR BATTERIES FOR TRANSPORTATION

The battery pack requirements for HEVs are different from those for PHEVs and EVs.[6] The DOE's program production price targets are \$500 to \$800 for HEV battery packs and \$1,700 to \$3,400 for the PHEV battery packs.

Material Needs and Raw Material Cost

The raw material needs and costs are based on a study by L. Gaines and R. Cuenza.[15] A standard cylindrical cell is the so-called "18650 cell" (18 mm wide and 65 mm long) which has a total mass of about 40 g (including inactive material and packaging) and a capacity of about 1.35 Ah.[16] The masses of material needed for HEV and EV battery cells are shown in Table I.

From Table I, one can estimate that a cell's capacity roughly scales with its mass. Although the packaging as a part of the whole for a large battery is smaller than for a small battery, the total mass of a 10 Ah cell is roughly 325 g and the total mass of a 100 Ah cell is roughly 3,430 g. Thus, the cost calculations for materials can be made by scaling up the costs of materials in an 18650 cell by a factor of 10 for HEVs and by a factor of 100 for EVs. Most battery designs result in batteries with a total of about 100 cells in a number of modules (such as 12 × 8, 10 × 10, or similar).

As an example, the materials costs for a $LiCoO_2$-based 18650 cell (including materials processing) can be estimated at about \$1.28 for the entire cell.[15]

Materials processing is very difficult to separate from materials cost and is therefore included in the materials costs in this section. In addition, the materials-processing cost changes dramatically with different materials and can therefore be considered material-specific. However, new processing techniques can lower the current high cost of raw materials.

Manufacturing and Labor Cost

State-of-the-art manufacturing of a cylindrical cell on a production line includes mixing and coating, calendaring and slitting, cutting, winding, tab welding, automated assembly, and inspection followed by testing, cycling, and packaging. To produce 100,000 units per year requires a total workforce of 76 to 104 people working on two lines in two shifts. Gaines and Cuenza[15] estimated the labor cost per cell and overhead costs to be $0.42 based on an 18650 cell.

Total Cost

The total 18650 cell costs add up to roughly $1.70. Scaling to HEV batteries results in $1,700 (twice the price target). There is no set cost target for EV batteries yet. However, based on this calculation, one could calculate a highly uncertain estimate of $17,000 per battery.

The estimate shows that to reach the goals, a tremendous effort is needed to reduce processing cost, material cost, and amount of needed material.

CONCLUSION

There is no doubt that lithium-ion cell chemistries offer some of the best options for electrical energy storage for high-power and high-energy applications such as transportation and stationary storage due to their electrochemical potential, theoretical capacity, and energy density. However, the estimated battery cost for the example HEV application is still twice the price target established by the USABC and DOE. With rising oil prices, a slightly higher price than the target might already receive enough consumer acceptance for a successful introduction into the market. However, the price still has to come down.

There are clearly needs in the areas of materials development, optimization, and processing. The calculations above separate between materials and labor costs. However, it is nearly impossible to separate raw material costs from material processing costs because we never use pure raw materials in the process; rather, we use material compounds that are suitable for the application and that are the least expensive in production. Additionally, even raw materials and material compounds have been processed. Thus, new low-cost processing methods for those materials and compounds have to be developed in order to minimize the battery's "raw material" cost.

Work is needed on hybrid technologies such as combining low-cost slurry-based techniques with treatment methods to replace tasks that are currently performed in two different steps. High-speed treatments, such as radiant processing, need to be optimized to replace slow furnace procedures. Investment costs and manufacturing times need to be minimized to make them feasible for battery applications. In addition, hybrid materials that can perform the functions of two or more components currently in use need to be developed and integrated into batteries (e.g., solid or high-viscosity electrolytes that do not need separators, have enhanced lithium exchange behavior, wet the electrode, and form a good bond).

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References

1. *World Batteries, Industry Study with Forecasts to 2010 & 2015* (Study #2095) (Cleveland, OH: Freedonia Group, 2006).
2. German Federal Ministry of Education and Research, "Innovation Alliance, Lithium Ion Battery 2015" (2008), *http://www.bmbf.de/de/11828.php*.
3. Oak Ridge National Laboratory calculations based on information from Energy Information Administration, U.S. Environmental Protection Agency, KEMA, and University of Delaware (2008).
4. D. Howell, *Energy Storage Research and Development, Annual Progress Report 2006* (Washington, D.C.: Office of FreedomCAR and Vehicle Technologies, U.S. Department of Energy, 2007).
5. FreedomCAR and Fuel Partnership and United States Advanced Battery Consortium, *Electrochemical Energy Storage Technical Team Technology Development Roadmap* (Southfield, MI: USCAR, 2006).
6. D. Howell, *Energy Storage Research and Development, Annual Progress Report 2007* (Washington, D.C.: Office of Vehicle Technologies, U.S. Department of Energy, 2008).
7. J. Goodenough, H.D. Abruna, and M.V. Buchanan, editors, *Basic Research Needs for Electrical Energy Storage* (Washington, D.C.: Office of Basic Energy Sciences, U.S. Department of Energy, 2007).
8. H.A. Kiehne, editor, *Battery Technology Handbook*, 2nd edition (New York: Marcel Dekker, Inc., 2003).
9. J. Besenhard, editor, *Handbook of Battery Materials* (Weinheim, Germany: Wiley-VCH, 1999).
10. N.J. Dudney and B.J. Neudecker, "Solid State Thin-Film Lithium Battery Systems," *Curr. Opin. Solid State Mat. Sci.*, 4 (5) (1999), pp. 479–482.
11. A.K. Shukla and T.P. Kumar, "Materials for Next-Generation Lithium Batteries," *Curr. Sci.*, 94 (3) (2008), pp. 314–331.
12. M.S. Whittingham, "Materials Challenges Facing Electrical Energy Storage," *MRS Bulletin,* 33 (4) (2008), pp. 411–419.
13. J. Newman and C. Monroe, "The Impact of Elastic Deformation on Deposition Kinetics at Lithium/Polymer Interfaces," *J. Electrochem. Soc.* 152 (2) (2005), pp. A396–A404.
14. P. Arora and Z. Zhang, "Battery Separators," *Chem. Rev.,* 104 (2004), pp. 4419–4462.
15. L. Gaines and R. Cuenza, *Costs of Lithium-Ion-Batteries for Vehicles* (Report ANL/ESD-42) (Argonne, IL: Argonne National Laboratory, 2000).
16. J. Carcone, "Update on Li-ion Batteries" (Paper presented at the 15th International Seminar and Exhibit on Primary and Secondary Batteries, Fort Lauderdale, Florida, 2–5 March 1998).

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