

# BATTERY POWER PRODUCTS & TECHNOLOGY

Solutions for OEM Design Engineers, Integrators & Specifiers of Power Management Products

## Battery Power for the Future

*Is the Energy Output of Batteries Reaching its Limit?*

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Small portable batteries have become a key consumer commodity. Just 50 years ago, flashlights were the main application for such batteries; now there is an almost uncountable number of portable battery-operated applications, such as laptops, cell-phones, medical devices, audio and security equipment and toys, to name just a few. It is not unusual for a household to have more than a dozen such devices, free from the power cord, requiring batteries for their operation.

While very dependent on batteries, the consumer is not satisfied with their size and weight and short operating life. The "need to press on with battery research" was highlighted by President Bush in his 2007 State of the Union address. Companies, such as Google, announced multimillion dollar programs in support of battery research. Critics point to the chip industry, to Moore's law and the doubling of performance every 18 months. Although advances have been made (as illustrated in Figure 1 that level of improvement cannot be achieved with batteries. To deliver their energy, the active materials in the battery must be consumed and there are limits to the amount of energy that is contained in these chemicals.

What can realistically be accomplished? A look at the factors influencing battery performance will help.

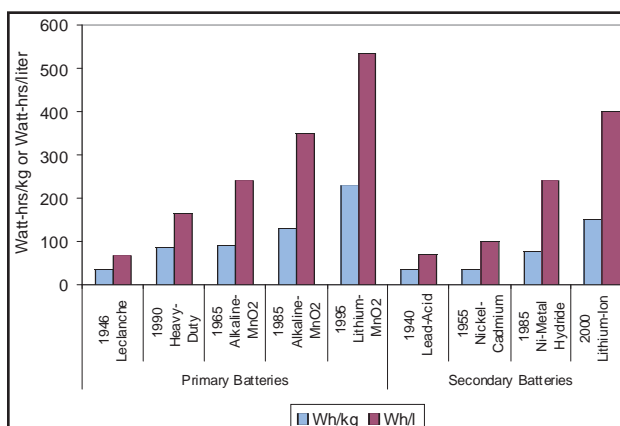


Figure 1. Advances in Battery Performance

The operation of a battery is simple. A battery consists of two major components: the anode electrode or "fuel" and the cathode electrode, the source of oxygen. In addition, a separator is needed to separate these two components and prevent the formation of an internal short circuit. An electrolyte is needed to provide the means for transfer of ions between the two electrodes for the reaction to take place. When the battery is being used, an electrochemical reaction takes place; the fuel is oxidized and the battery delivers its energy to the device it powers. The total amount of energy delivered is equal to the energy released by the reaction.

A listing of some of the major materials that can be used as active materials for the anode and cathode is given in Figure 2. The choice is limited as they must be relatively inexpensive, available in sufficient quantities for use in a commercial product and stable in the environment of the other materials in the battery. This figure shows the standard potential (voltage) that can be obtained and the electrochemical equivalence for each of these materials. The higher the standard potential and the higher the electrochemical equivalence (ampere-hours/gram), the higher the energy that can be obtained from that material.

	Material	Standard Reduction Potential (volts)	Electrochemical Equivalence (ampere-hours/gram)	
Anode Materials	Hydrogen	0.00	26.596	
	Lithium	-3.01	3.860	
	Magnesium	-2.38	2.200	
	Zinc	-0.76	0.820	
	Cadmium	-0.40	0.480	
	Lead	-0.13	0.260	
	Metal Hydride (MH)	-0.83	0.390	
	Carbon (LiC <sub>6</sub> )	-2.80	0.377	
	Methanol	---	5.020	
	Sodium Borohydride	---	3.000	
	Cathode Materials	Oxygen	1.23	3.350
		Fluorine	2.87	1.410
		Chlorine	1.36	0.756
		Manganese Dioxide	1.28	0.308
Nickel Oxylhydroxide		0.49	0.292	
Lead Dioxide		1.69	0.222	
Lithium Cobaltoxide (Li <sub>2</sub> CoO <sub>2</sub> )		1.25	0.150	
Lithium Iron Phosphate (LiFePO <sub>4</sub> )		0.42	0.170	
Lithium Mixed Transition Oxides (LiMn[1.5]Ni[0.5]O <sub>2</sub> )		2.00	0.130	
Carbon Monofluoride (CF <sub>2</sub> )		1.50	0.864	
Bismuth Fluoride		1.20	0.302	
Copper Fluoride		0.54	0.528	
Iron Fluoride		-0.21	0.712	

Figure 2.

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The active materials selected for the anode and cathode determine the voltage of the battery and the amount of these materials in the battery determine its energy output. The theoretical specific energy values for some of the commercial batteries, in terms of watt-hours per kilogram, based only on the weight of the anode and cathode and derived from the values given in Figure 2, are plotted, logarithmically, in Figure 3. A related parameter of interest, particularly for small batteries where volume is more significant than weight, is energy density (watt-hours/liter), which defines the amount of energy that can be contained in a given battery size.

Historically, zinc for primary and lead for rechargeable batteries have been and still are the most popular materials of choice for the anode. They are stable, low cost and when used as recommended, provide reliable service. The zinc Leclanche cell, originally developed more than 130 years ago, is still in use in its more recent heavy-duty design. In the early 1960s, the zinc/alkaline battery was developed, doubling the specific energy, providing higher power capability and having a much longer shelf life. This improved battery, with the development of the transistor, encouraged the growth of battery-operated radios, medical equipments and many other portable electronic devices. At the same time, a demand arose for portable rechargeable batteries to reduce operating costs and take advantage of their higher power capability. The lead-acid battery was found inadequate for the small sizes that were required for these applications. This led to the development of nickel-cadmium and later, nickel-metal hydride batteries.

But these improvements were not enough to meet the energy needs of laptops, cells phones and other devices as many new power consuming functions were added with the continued demand for smaller size, lower weight and longer operating times.

## Materials for Maximizing Energy Output

Lithium was always attractive as an anode material because of its high voltage and the highest electrochemical equivalent of any anode material, except for hydrogen. It was not used, however, because it was reactive with the aqueous electrolytes then available. In the 1960s, fairly low resistance organic electrolytes, providing adequate conductivity that were compatible with lithium were developed and the first lithium primary batteries were produced. As shown in Figure 1, these batteries delivered about twice the energy output of the zinc batteries and the advantage of a long shelf life of up to 10 years. Metallic lithium, however, proved to be unsatisfactory as the anode for rechargeable lithium batteries as a high surface area, very reactive form of lithium formed during recharging. This reactivity was reduced by the development of the lithium-ion battery in which the lithium is contained in an intercalation compound, with the lithium bound to a host. The battery, on charge, operates by transferring a lithium ion from the cathode host, typically a metallic transition metal, to the anode, most commonly a carbon. On discharge, the lithium ion is transferred from the anode to the cathode. They were initially called "rocking-chair" batteries as the lithium ions rock back and forth between the two electrodes. While the anode

used in the lithium-ion battery does not have as attractive electrochemical properties as lithium, it delivers more than twice the energy output of the earlier rechargeable batteries (Figure 1). More recently, the use of alloy anodes for these lithium batteries now offers significant hope for improvement in energy output. Silicon-graphite matrix anodes have demonstrated a reversible capacity of 640 mAh/gram versus 372 mAh/gram for carbon.

The lithium primary battery has been successful only in niche markets because of its higher cost. The lithium-ion battery, however, has been very successfully used in the tens of millions in cell phones, laptops and other portable electronics. It is being considered for use in applications requiring larger batteries and is the subject of much research and development to improve its performance.

Hydrogen also has attractive electrochemical characteristics. It is the subject of much R&D effort as part of the Hydrogen Economy program and the interest in a non-polluting hydrogen fuel cell for electric vehicles and other applications. It is now used in portable batteries as the anode active material in the nickel-hydrogen and nickel metal hydride batteries. The problems of handling hydrogen, because it is a flammable gas, are well known. For portable applications, while used in much smaller quantities, it still has to be contained in a pressure vessel, absorbed or chemically bound in a metal hydride to be used effectively. But, as shown in Figure 2, its attractive energy output is reduced considerably because of the need for a "container" as, for example, the metal hydride electrode.

The energy output of the cathode materials must also be considered in determining the energy output of the battery. Oxygen has very attractive values for electrochemical equivalence, but as a gas like hydrogen, it is used in most batteries as an oxygen containing compound. The values for these materials, some of which are listed in Figure 2, are much lower, which reduces the specific energy as well as the energy density that can be expected for these battery systems. Research on mixed transition metal oxides, such as  $\text{LiMn(1.5)Ni(0.5)O}_2$ , which provides 4.7 volts versus a lithium anode, indicates that still higher voltages can be obtained with lithium-ion batteries. The higher voltage and conductivity of these materials could result in higher energy, higher powered batteries.

Fluorine also has attractive electrochemical properties but, similar to oxygen, has to be used in the form of solid fluorine-containing solids. These metallic fluorides, such as  $\text{CuF}_2$ ,  $\text{FeF}_3$ , and  $\text{BiF}_3$ , have favorable characteristics but because of their poor electrochemical activity have not been used successfully. Recently, nanocomposites of these metal fluorides with conductive matrices have been shown to possess electrochemical activity and offer the opportunity for the development of batteries with higher energy output than currently available.

While most batteries are closed systems, some batteries, such as in the zinc/air battery, are open to the air and use ambient air for the oxidant. This potentially can reduce the size and weight of the battery as the active cathode material is not contained in the battery and introduced only as required. However, catalyzed electrodes, adequately sized to handle the required power, are needed to support the oxygen reaction. This adds to the volume and weight reducing some of the advantage. Air electrodes, lim-

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ited by the flow of air (unless forced by a fan or other means) even when catalyzed with precious metals, tend to operate at low rates. Direct exposure to the ambient environment, e.g. humidity, carbon dioxide, etc, also adversely affects performance. As a result, commercial ambient air batteries are mainly used in special low rate applications, such as hearing aids.

Over the last 200 years since Volta's invention of the voltaic pile, most, if not all, of the relatively large number of materials that can be used as anodes or cathodes in batteries have been explored. But only a few, mainly those listed in Figure 1, have attained wide commercialization and are in use today. Several others are used in limited quantities in niche markets. Most of the others failed to achieve successful commercialization. It will be difficult to find new materials that can be used successfully in batteries and have significantly higher theoretical energy content than those now in use. The values now attained for theoretical specific energy or energy density should be considered as close to the maximum, although continuing research may find new materials that will lead to batteries with higher energy content.

## Designs for Optimizing Energy and Power Output

A practical battery must also have a container and other materials of construction, such as seals, terminals, anode and cathode current collectors, electrolyte, separators and protective devices that add to the size and weight of the battery. Usually, the active anode and cathode materials are not electrochemically balanced and an excess of one is used to limit gassing and enhance safety, charging or other performance characteristics. Space has to be allowed in the cell for expansion of materials and to prevent leakage, increasing volume and lowering energy density. The weight and volume of these non-energy delivering materials can be at least equal to that of the active materials, reducing the specific energy and energy density to less than half of the theoretical values. For comparison, the theoretical values of the specific energy of a "practical" battery are also shown in Figure 3. The values are about 50 percent of the values shown for the active materials alone. For multicell batteries, these values can even be lower because of the weight and volume taken by the battery

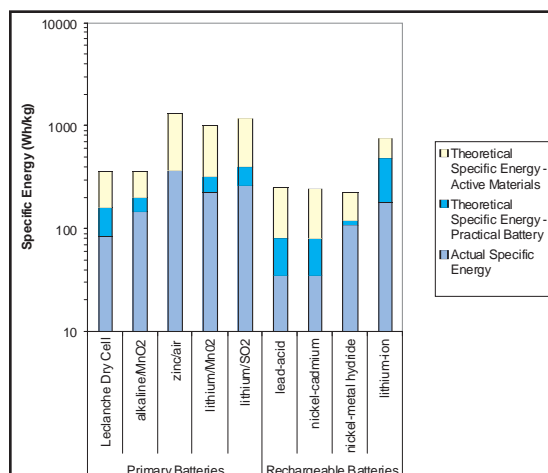


Figure 3. Theoretical and Actual Specific Energy of Battery Systems

container and by the protective devices that may be included.

Further, batteries do not operate at 100 percent efficiency. When a battery is discharged, the voltage is lower than its theoretical voltage. The difference is caused by losses due to cell and battery resistance and polarization of the active materials during discharge as illustrated in Figure 4. In the ideal case, the discharge proceeds at the theoretical voltage (Curve A) until the active materials are consumed and the voltage drops to zero. In practice, the discharge curve is similar to Curve B. The initial voltage is lower than the theoretical voltage due to internal cell resistance and polarization effects at both electrodes. During discharge, the voltage drops further as the cell resistance increases due to accumulation of discharge products, activation and concentration polarization and related factors. The discharge is terminated at some practical "end" voltage, a value well above zero volts. Thus, not all of the available active material is used, further reducing the energy output.

The actual specific energy output of the various battery systems, based on the batteries being discharged under moderate or mostly optimum conditions is also shown in Figure 3. In practice, less than 30 percent of the original theoretical specific energy is available for most systems

Under more stringent discharge conditions such as high discharge rates and lower temperatures, the useable energy output is further reduced. This is also illustrated in Figure 4 as Curve C, which is similar to Curve B but represents a discharge under more severe conditions. The voltage is lower throughout the discharge and the end voltage is reached earlier. The net result is that only about 25 percent or less of the theoretical specific energy of the active materials is actually delivered.

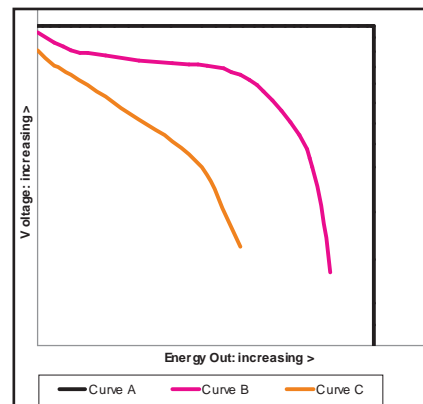


Figure 4. Characteristic Discharge Curve

During the lifetime of a battery system as manufacturers and users gain experience with the product, there are many options to modify designs and chemistry to improve performance. As non-active materials account for about 50 percent of the weight and volume of the battery and internal cell resistance is responsible for a significant amount of energy loss, the focus is to reduce these components without impairing other performance characteristics such as safety, cycle life, shelf life and capacity loss.

Manufacturers are using thinner-walled containers and enclosing batteries in foil laminate packaging to reduce the weight and volume associated with the inert components. Other light-weight components, such as metal foam current collectors, are also being utilized. Batteries can be designed to enhance certain characteristics like high capacity, high power capability and high temperature operation. Batteries designed for low rate applica-



tions (as are most of the standard primary batteries) generally use a bobbin construction to maximize the amount of active materials that can be put into the battery. This maximizes the amount of available energy but limits the rate at which this energy can be efficiently discharged. Batteries designed for high power applications, including those designed for rapid charging, must use structures that minimize internal resistance and provide more sites for chemical reaction. To do this, these batteries may use a spiral-wound (jelly-roll) construction, a multiple parallel plate structure or other techniques to minimize the space between the electrodes and maximize surface area. High conductivity electrolytes, additives such as carbon blacks or graphite in the electrodes, current collectors and tabbing can be chosen to further minimize internal resistance and heating effects.

The biggest challenge is meeting the demand for safe, lightweight, high power batteries, packed to deliver maximum service with thin separation between electrodes. The thin internal constructions have to be designed to prevent internal shorting. High rate charging and discharging cause the batteries to operate at high temperatures and require controls, fusing or means to cut-off cell reaction to prevent overheating, thermal runaway or fire. New designs and techniques are being proposed to overcome these problems, such as using nanotechnology or newer materials such as the lithiated olivine compounds (e.g. lithium iron phosphate), which decompose at much higher temperatures than the transition metal oxides and thus enhance safety. But, the need to run batteries at high power levels because of the requirements of the equipment and exacerbated by the demand for smaller and lighter batteries, results in their operating under very inefficient conditions.

Significant improvements in performance can be attained during the life time of a battery system, but as a system matures, the improvement in performance levels off. While there are opportunities to improve certain performance, particularly in the area of high power batteries for specific applications, significant advances in energy density or specific energy of a battery system are unlikely to occur with mature technologies.

## Fuel Cells

Though still under development, fuel cells are also being considered for portable applications, in place of batteries, offering the possibility of longer service life. For these small applications, the use of hydrides as a source of hydrogen or other "fuels", such as methanol, are being considered. Ambient air is used as the source of oxygen. A fuel cell differs from a battery, which is self-contained. In the fuel cell, the fuel is fed into the fuel cell as it is used. Thus, a fuel cell consists of two parts: the electrochemical converter and the source of fuel. This design is penalized as the converter, sized to handle the required power level, must be part of the device regardless of how long the device has to operate. The fuel cell becomes advantageous for longer service times as only fuel, which should have a more favorable specific energy density than the battery, has to be added to extend operating time.

This is illustrated in Figure 5, which compares the weight of the fuel cell with the alkaline primary battery and the lithium-

ion rechargeable battery, each system delivering 5 watts for various periods of time. At short service time, the weight of the fuel cell converter (projected at 250 grams) predominates and the fuel cell system has the highest weight. For

longer service, the performance of the fuel cell depends mainly on the weight of the "fuel" (projected, in this case, for methanol at 500 mWh/gram) and the advantage of the fuel cell over the batteries becomes evident, provided that the specific energy of the fuel is greater than that of the battery with which it is compared). The performance of the lithium-ion battery (estimated specific energy of 180 mWh/gram) plots with a steady slope as it maintains about 90 percent of its specific energy even as the discharge rate increases to higher power levels. The performance of the general purpose alkaline primary battery, designed to optimize performance at the lower discharge rates with a specific energy of 170 mWh/gram, tapers off at the higher rates.

Specific batteries and fuel cells, having characteristics different from those plotted, may result in different cross-over points but the same relationships should hold. Similarly the relationships are the same if the comparison is considered on the basis of volume or energy density. The design of a fuel cell, for example for cellphones, with the emphasis on small size and weight may prove to be difficult unless the user is willing to accept a larger unit to obtain the longer service. A more acceptable trade-off may be found for larger portable devices, such as the lap-top, once the development of these portable fuel cells is completed.

## The Future

While not meeting all of the desires and demands of consumers, who are seeking smaller size and longer service time, batteries will continue to be a major factor contributing to the success of portable electronic devices. There is no other viable alternative power source for these portable applications that is available today.

Realistically, it is becoming increasingly difficult to develop new battery systems that will have significantly higher energy output and still meet the requirements of a successful commercial product including availability of materials, reasonable cost, safety and environmental acceptability. The introduction of the lithium primary battery systems more than 25 years ago and the lithium-ion rechargeable battery technology in the 1990s were

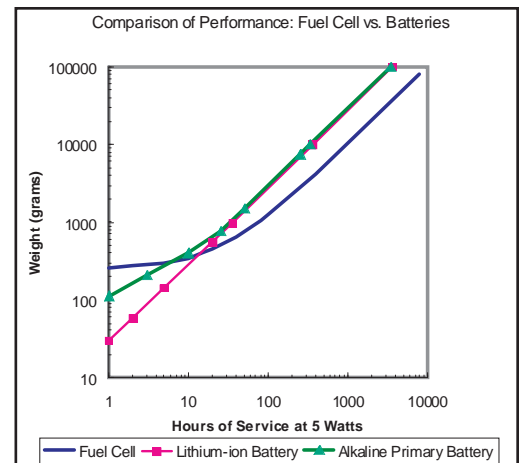


Figure 5. Comparison Performance: Fuel Cells vs. Batteries

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the last major advances in battery technology. These may represent the best that can be achieved with battery systems. Most materials that can be used as the active materials have been investigated and further improvements in battery technology will require breakthrough discoveries. The impact of the fuel cell on the design of portable electronic devices awaits its successful development.

For this time, then, the values listed below are close to the maximum that can be expected for the energy output of portable batteries:

	Primary Batteries-closed systems (30 hour rate)	Primary Batteries-using ambient air (100+ hour rate)	Rechargeable Batteries (5 hour rate)
Specific Energy (Watt-hours/kilogram)	720	400	225
Energy Density (Watt-hours/liter)	1,270	1,300	525

It must also be recognized that even if the breakthroughs occur through the development of new materials, designs that utilize a higher percentage of the available theoretical energy or other advances, because of the thermodynamic limitations to battery performance, these values will probably not be exceeded by more than 50 to 100 percent.

For further improvement of battery performance in small electronics, it defaults to the electronic industry to continue their remarkable advances that do not have such limitations, at least in the immediate future. Power demands of their electronics must be reduced. In fact, Intel and IBM recently announced improvements in the insulating material used in integrated circuits that will reduce their power requirements.

Efficiency of power supplies must be increased. Devices must be designed to insure that the batteries are used optimally and accept the trade-offs that are needed to utilize the energy output of batteries safely and optimally.