Electrochemical Capacitors: Challenges and Opportunities for Real-World Applications

by John R. Miller and Andrew F. Burke

People today are very familiar with different battery technologies, from small zinc-air button cells to AAA alkali cells to spiral wound lithium-ion laptop batteries to fifty-pound lead acid batteries found in automobiles. This situation has come about because people rely heavily on battery power.[1] Common battery applications include, for instance, power for cell phones, Sony Walkman, PDAs, laptop computers, Ipod players, digital cameras, and on and on. In sharp contrast, people today are much less familiar with capacitor technologies, although capacitors also store energy. One reason for this is that capacitors have exceptionally long life and seldom need service while batteries, bar none, eventually need charging or replacement. The aim of this article is to express in a clear fashion the differences between battery and capacitor technologies, identify several applications that exploit one or more characteristics unique to electrochemical capacitor energy storage, and finally point out some key technology challenges for their further development and greater market acceptance.

Background

An electrochemical capacitor (EC), sometimes called a supercapacitor or an ultracapacitor, stores electrical charge in the electric double layer at a surface-electrolyte interface, primarily in high-surface-area carbon. Because of the high surface area and the thinness of the double layer, these devices can have very high specific and volumetric capacitances. This enables them to have very high energy density for capacitors and essentially unlimited charge/discharge cycle life. The operational voltage per cell, limited only by the breakdown potential of the electrolyte, is usually <1 or <3 volts per cell for aqueous or organic electrolytes respectively.[2]

The concept of storing electrical energy in the electric double layer that is formed at the interface between an electrolyte and a solid has been known since the late 1800s. The first electrical device reported to use double-layer charge storage was not commercialized.[3] Standard Oil Company of Ohio (SOHIO) invented in 1966 the device in the format now commonly used,[4,5] which forms the basis for the hundreds of subsequent patents, the thousands of journal articles, and several annual specialized meetings.[6] EC technology has grown into an industry with sales of several hundred million dollars per year that is poised for rapid growth in the near term[7] due to expansion of power quality needs and the emerging energy management/conservation applications.

Following the commercial introduction of NEC's SuperCapacitor™ in 1978 under license from SOHIO, ECs have evolved through several generations of designs.[8,9] Initially they were used as backup power devices for volatile clock chips and complementary metal-oxide-semiconductor (CMOS) computer memories. Many other applications have emerged over the past 30 years, including wireless communication, power quality, and improved energy efficiency via regenerative energy capture processes, for instance in hybrid electric vehicles. Overall, the unique attributes of ECs often complement the limitations of other power sources like batteries and fuel cells.[10,11]

Early electrochemical capacitors were rated at a few volts and had capacitance values measured from fractions of farads up to several farads. The trend today is for cells ranging in size from small millifarad-size devices with exceptional pulse power performance up to devices rated at several kilofarads. Some specialized EC cells now in production for traction applications have ratings of more than 100 kF.[12] The technology is experiencing increasingly broader use, both replacing batteries in some cases, and in others complementing their performance. In a few situations ECs have been an enabling technology.

Capacitor Technology vs. Battery Technology

It is important to keep firmly in mind the basic differences between electrochemical capacitors and batteries both in their materials/structures and in the different physical/chemical mechanisms involved in how they function.[13] The battery stores energy chemically and has much higher energy density than a capacitor, but it also undergoes physical change between the charged state and the discharged state. The capacitor, on the other hand, stores its charge physically, and it experiences no major change in the structure of the material with charge state. These points of comparison allow us to focus on two equally basic differences in the functioning of these technologies that make replacing one with the other far less plausible than one might expect.

Because of their differences in structure, there is first of all a fundamental difference between the two technologies in terms of charge/discharge time. This time for electrochemical capacitors is on the order of a few seconds or less. The energy stored in an EC can be released within that time frame, and it can, as well, be recharged in the same time. Lithium ion batteries, on the other hand, even the high-power devices recently commercialized, or most any battery for that matter, take several minutes or more time to release all their energy, and similarly several minutes to tens of minutes to hours to be recharged. Both ECs and batteries can be utilized with only partial charge or partial discharge operation, which is also of interest for many applications.

The second fundamental difference caused by the energy storage mechanisms is seen in the cycle life of the two technologies. Although great advances have been made in battery technology, the chemical changes that take place suggest nevertheless that their cycle life for deep discharge will always be limited. Some current batteries claim to provide 5,000 or more such cycles, but this is small in comparison to that of capacitors, whose cycle life is typically measured in hundreds of thousands to millions of cycles. When batteries are utilized in the pulse mode, their cycle life can be hundreds of thousands of cycles, but only when a small fraction of the total stored energy is added and removed each cycle.

These differences become critical when attention is turned to thermal management. In many applications, particularly ones involving heavy hybrid vehicles, the charge/discharge cycles are rapid and involve very high power levels. For capacitors, their charge/discharge efficiency is high and the energy lost to heat during each cycle[14] is relatively small and readily removed. The energy lost to heat in the batteries is a much larger amount, making heat removal more crucial and its extraction costs much higher.

A final issue rooted in the material/structural differences is safety. ECs generally age gracefully, their performance declining gradually in a predictable fashion without catastrophic events. Batteries, on the other hand, do not always age so benignly but can do

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Table I. Comparison of some important characteristics of state of the art electrochemical capacitors and lithium-ion batteries.

Characteristic	State of the Art Lithium Ion Battery	Electrochemical Capacitor
*Charge time	~3-5 minutes	~1 second
*Discharge Time	~3-5 minutes	~1 second
Cycle life	<5,000 @ 1C rate	>500,000
Specific Energy (Wh/kg)	70-100	5
Specific power (kW/kg)	**0.5 -1	5-10
Cycle efficiency (%)	<50% to >90%	<75 to >95%
Cost/Wh	$1-2/Wh	$10-20/Wh
Cost/kW	$75-150/kW	$25-50/kW

** Time for discharge and charge of the useable total energy stored in the devices.*
*** Power capability of the battery for short duration partial discharge at 90% efficiency.*

so considerably more catastrophically, the worst-case being a thermal runaway situation that can lead to a fire.

Table I compares state of the art commercial lithium-ion battery technology with electrochemical capacitor technology in several important ways. Cost figures were based on today's product prices for cells in large quantities, each normalized to mass using dc energy values and power levels at which charge/discharge efficiency is at least 90%.[15]

It is clear that the charge/discharge times and the cycle life of the capacitor and battery technologies are quite different today, and it is expected that this situation is not likely to change in the foreseeable future. Hence the suitability of each technology for particular applications is now and will remain markedly different regardless of likely advances that may be made in either of the technologies. The next section discusses several applications that use energy storage which reveal how charge/discharge time and cycle life differences affect the applicability of the two technologies.

Electrochemical Capacitor Applications

Application 1: Energy Management/Conservation Applications

Seaport Crane.—The fact that capacitor systems are cost-effective (their cost can be recovered in only a few years) is attested to by their increasingly broad use in rubber-tired gantry cranes being used to load and unload container ships at major seaports in the Far East.[16] One important function of capacitors in this application is to capture energy that would otherwise be wasted as heat in the repetitious up and down movement of heavy shipping containers. A second important function of the capacitor system is to allow a size reduction in the primary power source, usually a diesel engine. This is possible when the capacitor is sized to meet the peak power demand and the engine is sized to operate at an average power level. Importantly, this hybrid operating system, like hybrid electric vehicles, can substantially reduce emissions and thus improve air quality. Figure 1 shows an example of a hybrid diesel-electric gantry crane using EC energy storage.

Today's advanced batteries, without serious derating, do not have the required high power capability for efficient operation nor adequate cycle life for this application. The next example helps to quantify these limitations of batteries for this type of application.

Heavy Hybrid Vehicles.—Electrochemical capacitors are among the most promising of the energy storage technologies currently in use or being considered for use in heavy hybrid vehicles. They are particularly well suited for city transit buses (Fig. 2) with stop-and-go driving;[17] in trash trucks, which can experience as many as a thousand start/stop cycles during a day; and in delivery trucks, which operate on similar drive cycles.

The primary challenges for any energy storage unit used in heavy hybrid vehicles are the high cycle life required and the need to dissipate the heat generated due to charge/discharge losses. Electrochemical capacitors have very high efficiency and have been designed with thermal management in mind thus making them well suited for heavy hybrid vehicle applications.

The major difference in the use of electrochemical capacitors and high power batteries in hybrid vehicles is shown in Fig. 3, which compares captured and stored regenerative energy for two storage units—a 3000 F, 2.7 V electrochemical capacitor and a 12 Ah Li-ion battery.[15] The test was performed by measuring the amount of energy captured by each device for various constant-current charge times. For both cases, the stored regenerative energy was the amount of energy that could be discharged after the charge. Charging was to the manufacture-recommended upper voltage limit, which was 2.7 V for the capacitor and 2.8 V for the battery. The capacitor initially was at 1.35 V and the battery at 10% state of charge.

Fig. 1. *Hybrid diesel/electric rubber tired gantry crane with an electrochemical capacitor energy storage system. This crane is used for loading and unloading container ships. The capacitor system captures and stores regenerative energy during load lowering that is then used to help raise the next load, resulting in improved efficiency and greatly reduces air emissions. (Photo courtesy of Nippon Chemi-Con Corporation.)*

Fig. 2. *Hybrid city transit bus that uses an electrochemical capacitor energy storage system. Typical charge/discharge periods may be forty seconds in this application with continuous 16-hours-per-day operation (>1000 charge/discharge cycles each day). (Photo courtesy of ISE Corporation.)*

As shown in Fig. 3, with charging times greater than 600 s (10 minutes) the battery has a constant ~15 times higher specific energy than the capacitor. It clearly would form the lightest storage system in an application having this charge time. At shorter charging times, the battery shows reduced specific energy, for instance with a 100 s charge, the battery captures only ~5 times more energy than the capacitor. And for 10 s charge time, the two devices capture the same specific energy, but the capacitor can discharge ~95% of this amount while the battery can discharge only ~50% of the amount. Thus with 10 s charging time, the effective energy density of the capacitor is twice that of the battery. Furthermore, the battery will need a considerably larger cooling system to remove the dissipated energy. Notice that the capacitor's specific energy line (stored energy) remains flat well below 10 s, further amplifying the differences in charge/discharge characteristics of the two technologies. That is the reason why batteries are not well suited for high-rate cyclic operation. If used in this way, only a relatively small fraction of the battery's energy can be utilized and its effective energy storage capacity and energy density are much lower than the rated values.

Hence in a heavy hybrid application, the typical design approach is to greatly oversize the battery. In effect, oversizing shifts battery charge times to the right in Fig. 3. Thus when battery derating is taken into account, the volumetric storage between the two technologies is not very different, thus disproving to a considerable degree the common view about the marked superiority of batteries in terms of energy density. ECs are well suited for heavy hybrid vehicles as demonstrated by the hundreds of hybrid-electric city transit buses loaded with banks of electrochemical capacitors that are currently in successful operation.

Application 2: Day-Night Storage

Capacitors have also been proposed for bulk energy storage to store off-peak electricity from the utility grid at night, when it is abundant and low cost for use during the day, when it may be in short supply and more costly. This is particularly interesting for hot summer days, when there are heavy air conditioning loads on the grid system. Night storage/day use like this would involve only a single cycle per day, meaning a storage system designed to last for ten years would require fewer than 5,000 cycles, a number readily attainable by ECs but a challenge for most batteries.

A capacitor suitable for this application is an asymmetric EC with a lead oxide positive electrode and an activated carbon negative electrode.[18] This device can have an energy density of ~20 Wh/kg, nearly that of a high power lead-acid battery, but with much higher cycle life. The key to this application is the low cost of the device compared to carbon/carbon devices. The system must be designed not only to meet necessary life requirements, but it must do this such that the stored electricity being added back to the grid is no more costly than new electricity being generated at that very moment.[19] A successful realization of this bulk storage concept could mean that ~20% of the energy needed during the day would be energy stored from the evening before. This equates to a higher utilization of the capital investment of the utility company, and it likewise translates into more efficient use of the distribution system.

The economics of the lead-carbon asymmetric capacitor may allow it to join with pumped hydro as a viable means for storing off-peak electrical energy. (Pumped hydro involves lifting water to an elevated reservoir during the night to generate hydroelectricity by flowing back down the next day. There are many tens of such installations in operation today around the world with more than 90 GW of pumped storage.[20]) The significant advantage of capacitor storage over pumped hydro storage is that it can be located anywhere, even in the middle of a city if desired.

EC electricity storage may first be used at the end of overloaded distribution lines since a delay in constructing upgraded lines favors storage system economics. Capacitor technology for this application has advanced in recent

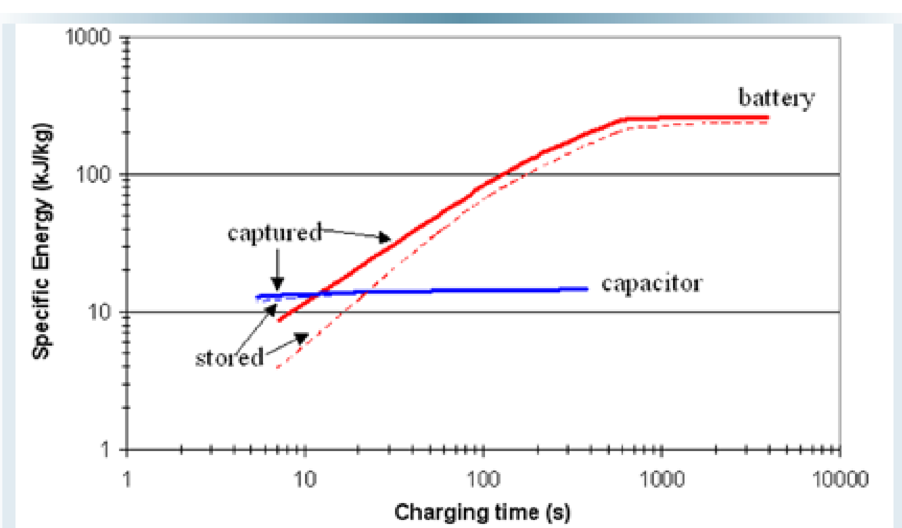

Fig. 3. *Captured and stored regenerative specific energy for two different energy storage media—a 3000 F, 2.7 V electrochemical capacitor cell and a high-rate 12 Ah, 2.8 V lithium-ion battery cell. Note that both have equal regenerative energy storage with ~20 s charging times. The capacitor has higher specific regenerative energy storage at all charge times less than ~20 s.*

Fig. 4. *Capacitor powered screwdriver that is fully charged in 90 seconds. This product is aimed primarily at the home "do-it-yourself" market where battery powered tools are invariably discharged due to their infrequent use and also require longer times to prepare for operation.*

years to where it now appears technically ready for commercialization.[21,22] The economics are becoming increasingly viable, particularly because of today's higher energy costs and the greater attention given to reducing greenhouse gases.

Application 3: Power Tools

A cordless electric screwdriver, capable of being fully charged in only 90 seconds, was recently introduced. Electrochemical capacitors power this product and were selected rather than batteries because of their power delivery performance, cycle life, and fast charge capability, which greatly exceed that of batteries. Although batteries can store considerably more energy than a capacitor, they generally have useable charge/discharge times that are too long and thus only a fraction of their stored energy can be used effectively. Even today's most advanced lithium ion batteries typically require ten minutes or longer charging times.

The screwdriver (Fig. 4) contains six 100 F, 2.7 V EC cells, having about 1.5 kJ of stored energy. A high-rate lithium ion battery of the same dimensions would store perhaps 20 times more energy. The screwdriver with capacitor energy storage does require more frequent charging than the battery system, but the charging is of very short duration. This means that the capacitor-powered screwdriver may in fact perform work at a higher average level, for instance, by the home repair person. Owing to infrequent use, portable screwdrivers are often in a state of either only partial charge or even full discharge. The first step of any project is thus charging the screwdriver, which can take 10 minutes or longer with a battery. With a capacitor system, however, the screwdriver is ready in 90 seconds, perhaps even sooner if only brief use is projected.

Another cordless tool that exploits the power performance of electrochemical capacitors is a power tubing cutter produced by the Superior Tool Co. for cutting copper tubing. It has ECs wired in parallel with the rechargeable battery to boost its efficiency, a configuration most helpful in powering the 2-4 seconds of operation required for cutting.[23] Adding a capacitor to a battery makes it possible for a substantially greater number of tubes to be cut on each battery charge.

Technology Challenges

For many applications, the relatively high cost of ECs is currently the primary reason they are not the energy storage technology of choice. Despite their high level of performance, electrochemical capacitors are simply too expensive to compete against the other available approaches. For some applications, potential users find ECs of interest but conclude that their energy density too low. Hence increasing energy density and lowering cost are the primary challenges facing EC developers. This must be done without sacrificing the high cycle life and exceptional high rate performance that sets ECs apart from batteries.

Increasing the voltage at which the EC can operate reliably is highly desirable owing to the V^2 term in the stored energy, resulting in higher energy density. This would also increase the power performance, which is again proportional to V^2. A higher operating voltage would also reduce costs in several different ways. A higher energy density would mean that the contribution of packaging, separators, and even electrolyte would be less because there is more stored energy for the same quantity of carbon, the active ingredient. Higher cell voltage also means that fewer cells in series are needed for a specified system voltage. This would reduce the burden of external voltage-balance circuits now often used. There is further a potential improvement in reliability occasioned by the fact that the higher operating voltage makes it possible for fewer components to be involved in creating a system.[24] A comprehensive report was recently published by the Office of Basic Science of the U.S. Department of Energy that describes state-of-the-art for both battery and electrochemical capacitor electrical energy storage technology.[25] It clearly identifies priority research directions for both technologies that, if followed, should lead to major performance improvements in both. ■

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