# Electrochemical Capacitors for Energy Management

Rapid storage and efficient delivery of electrical energy in heavy-duty applications are being enabled by electrochemical capacitors.

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Energy storage technology is a key element in harvesting the kinetic energy that is wasted whenever vehicles or large machines must be slowed or stopped. Although batteries have been successfully used in light-duty vehicles, hybrid platforms for trucks and buses will require storage and delivery of much higher currents than can be accommodated readily by batteries. Unlike batteries, electrochemical capacitors (ECs) can operate at high charge and discharge rates over an almost unlimited number of cycles and enable energy recovery in heavier-duty systems.

Like all capacitors, ECs (also called supercapacitors or ultracapacitors because of their extraordinarily high capacitance density) physically store charge. Conventional electrostatic and electrolytic capacitors store charge on low-surface-area plates, but ECs store charge in an electric double layer set up by ions at the interface between a high-surface-area carbon electrode and a liquid electrolyte (*1*, *2*). ECs first appeared on the market in 1978 as farad-sized devices to provide computer memory backup power.

A simple EC can be constructed by inserting two conducting rods in a beaker of salt water. During charging, charge separation occurs at each liquid-solid interface and potential builds up between the rods. Solvated ions in the electrolyte are rapidly attracted to the solid surface by an equal but opposite charge in the solid. These two parallel regions of charge are the source of the term "double layer." This process in effect creates two capacitors, connected in series by the electrolyte, that stay charged after the circuit is opened. Because the surface area of activated carbon electrode material can be thousands of square meters per gram, a 5000-farad EC (a million times the capacitance offered by typical electrostatic or electrolytic capacitors) can be small enough to be handheld.

This very high capacitance comes at a cost: The operating voltage of an EC cannot exceed the potential at which the electrolyte undergoes chemical reactions (typically 1 to 3 V per cell). For high-voltage applications, EC cells, like batteries, can be series-connected.

One of the most important advantages of batteries over ECs is that for a given volume, they can store 3 to 30 times more charge. However, ECs can deliver hundreds to many thousands of times the power of a similar-sized battery. In addition, the highly reversible electrostatic charge storage in ECs does not produce the changes in volume that usually accompany the redox reactions of the active masses in batteries. Such volume changes are the main cause of


**ECs at work.** Hybrid diesel/electric rubber-tired gantry crane with DLCAP electrochemical capacitor energy storage system (fuel savings of 40% are typical).

| Property | Battery | Electrochemical capacitor |
|---|---|---|
| Storage mechanism | Chemical | Physical |
| Power limitation | Reaction kinetics, mass transport | Electrolyte conductivity |
| Energy storage | High (bulk) | Limited (surface area) |
| Charge rate | Kinetically limited | High, same as discharge rate |
| Cycle life limitations | Mechanical stability, chemical reversibility | Side reactions |

Comparison of properties of rechargeable batteries and electrochemical capacitors.

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the limited cycle life of batteries (generally several hundred to a few thousand cycles), compared to demonstrated full charge-discharge cycles for ECs into the many millions. The major differences between rechargeable (secondary) batteries and ECs, and their important fundamental properties, are compared in the table.

An important related class of energy storage devices are pseudocapacitors, which undergo electron transfer reactions but behave like capacitors. These materials store energy through highly reversible surface redox (faradic) reactions in addition to the electric double-layer storage. Materials that exhibit such pseudocapacitive storage (*1*) range from conducting polymers to a variety of transition metal oxides (*3*–*5*). The $RuO_2$ pseudocapacitor has the highest specific capacitance (~1000 F/g) in this class, but is prohibitive in price (a vehicle-sized EC of $RuO_2$ would cost more than $1 million). Efforts to develop more practical pseudocapacitive materials are now quite active.

The second generation of ECs used symmetric designs and organic electrolytes—typically an ammonium salt dissolved in an organic solvent such as propylene carbonate—which increased the rated cell voltage from under 1 V to ~2.5 V per cell. The most recent EC designs, which date from Russian patents in the mid-1990s, are asymmetric. One electrode is identical to those used in symmetric ECs, whereas the other is battery-like (relying on electron charge transfer reactions) but has much greater capacity and higher operating voltage. Asymmetric capacitors with specific energies of >10 watts-hour/kg are commercially available (*6*) and are well suited for transportation (traction) applications. Charging times for such systems are ~10 min.

Several asymmetric EC designs under development (*7*–*9*) use a lithium-ion intercalation electrode with an activated carbon electrode in an organic electrolyte (*7*) or an activated carbon electrode with a lead dioxide battery-like electrode and sulfuric acid as the electrolyte, with the potential of specific energies in excess of 20 watts-hour/kg at very low cost (*8*). Each of these designs can provide high cycle life relative to that of a battery because of the electrode capacity asymmetry. Capacity asymmetry reduces the depth of discharge of the battery-like electrode, thereby increasing its cycle life and power performance.

Symmetric ECs with specific energies of ~5 watts-hour/kg and response times of 1 s are widely available and can be used to store and release regenerative braking energy efficiently in vehicles and industrial equipment. They can also be used for load leveling—delivering power above the average value provided by a distributed generator (such as a fuel cell) and storing excess energy when power levels are below average.

Although lithium-ion batteries have advanced greatly in recent years, they still require 3 to 5 min for charging, versus ~1 s for an EC. Thus, battery systems generally must be grossly oversized in such applications to improve their efficiency and to lengthen their cycle life. Also, ECs are generally much safer than batteries during high-rate charge and discharge.

Finally, ECs are being used across a vast swath of commercial and industrial equipment. One example is a seaport rubber-tired gantry crane (see the figure) that has a capacitor system to store energy during load lowering. The use of ECs has reduced its energy usage by 40%.

**References and Notes**


1. B. E. Conway, in *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications* (Kluwer Academic/Plenum, New York, 1999).
2. J. Chmiola *et al*., *Science* **313**, 1760 (2006); published online 16 August 2006 (10.1126/science.1132195).
3. I. D. Raistrick, R. J. Sherman, in *Proceedings of the Symposium on Materials for Energy Conversion and Storage*, S. Srinivasan, S. Wagner, H. Wroblowa, Eds. (Electrochemical Society, Pennington, NJ, 1987), pp. 582–593.
4. M. Mastragostino, K. Arbizzani, F. Soavi, *Solid State Ionics* **148**, 493 (2002).
5. M. S. Hong, S. H. Lee, S. W. Kim, *Electrochem. Solid State Lett*. **5**, A227 (2002).
6. Available from JSC ESMA, OKB FIAN, Troitsk 142190, Russia (www.esma-cap.com).
7. T. Morimoto, paper presented at the International Conference on Advanced Capacitors, 28 to 30 May 2007, Kyoto, Japan.
8. S. A. Kazaryan *et al*., *J. Electrochem. Soc.* **153**, A1655 (2006).
9. A. Balducci *et al*., *Electrochim. Acta* **50**, 2233 (2005).