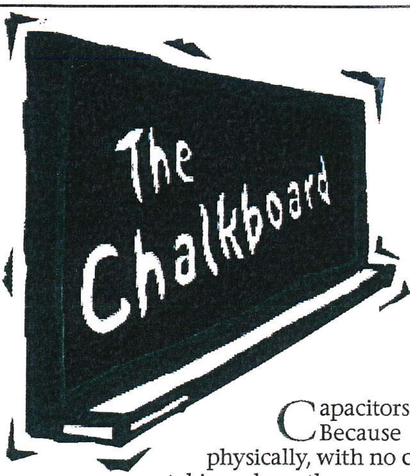


SUPERCAPACITORS

FUNDAMENTALS OF ELECTROCHEMICAL CAPACITOR DESIGN AND OPERATION

by John R. Miller and Patrice Simon

Capacitors store electrical charge. Because the charge is stored physically, with no chemical or phase changes taking place, the process is highly reversible and the discharge-charge cycle can be repeated over and over again, virtually without limit. Electrochemical capacitors (ECs), variously referred to by manufacturers in promotional literature as "supercapacitors" or "ultracapacitors," store electrical charge in an electric double layer at the interface between a high-surface-area carbon electrode and a liquid electrolyte.[1,2] Consequently, they are also quite properly referred to as electric double layer capacitors.

A simple EC can be constructed by inserting two conductors in a beaker containing an electrolyte, for example, two carbon rods in salt water (Fig. 1). Initially there is no measurable voltage between the two rods, but when the switch is closed and current is caused to flow from one rod to the other by a battery, charge separation is naturally created at each liquid-solid interface. This effectively creates two capacitors that are series-connected by the electrolyte. Voltage persists after the switch is opened—energy has been stored. In this state, solvated ions in the electrolyte are attracted to the solid surface by an equal but opposite charge in the solid. These two parallel regions of charge form the source of the term "double layer." Charge separation is measured in molecular dimensions (*i.e.*, few angstroms), and the surface area is measured in thousands of square meters per gram of electrode material, creating 5 kF capacitors that can be hand-held.

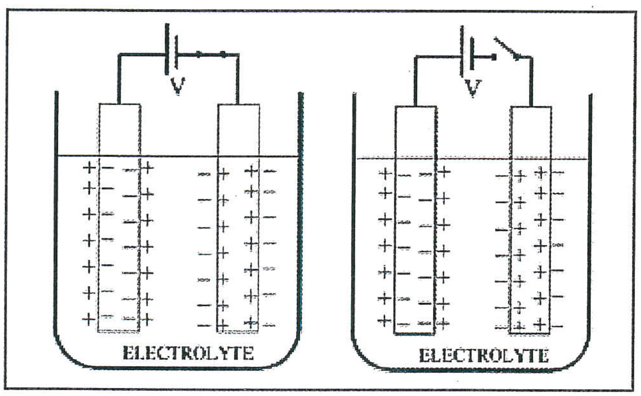


Fig. 1. *Electric double layer capacitor constructed by inserting two electrodes in a beaker and applying a voltage. The voltage persists after the switch is opened (right), creating two series-connected capacitors. Charges in the electric double layer are separated by only about 1 nm.*

The very feature of an electrochemical capacitor that makes such high capacitances possible, namely the highly porous high-surface-area electrodes, is also the reason for the relatively slow response of these devices compared to conventional capacitors. To illustrate the reason, Fig. 2 shows an idealistic representation of a cross-section of a pore in a nanoporous carbon material, where it is shown as a cylinder filled with electrolyte and in which an electric double layer covers the interior wall surface of the pore.[3] Electrical connections to the stored charge are made through the solid carbon surrounding the pore and through the electrolyte from the mouth of the pore, electrolyte conductivity being much less than carbon conductivity. Charge stored near the pore mouth is accessible through a short path with small electrolyte resistance. In contrast, charge stored deeper within the pore must traverse a longer electrolyte path with a significantly higher series resistance. Thus, the overall response can be represented by a multiple-time-constant equivalent circuit model.[4-6] Irrespective of this behavior, the response time of an electrochemical capacitor in both charge and discharge operation is extremely short, about 1 second, as compared to batteries (minutes to tens of minutes).

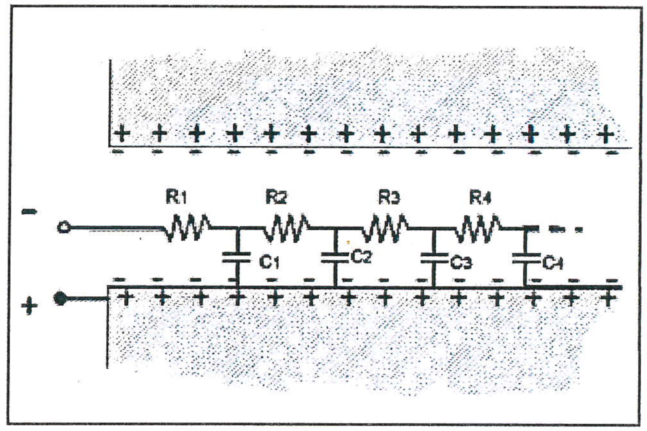


Fig. 2. *Idealistic representation of an electrolyte-filled right-cylindrical nanopore in a carbon electrode of an electrochemical capacitor showing the distributed resistance from the electrolyte and distributed charge storage down the interior surface of the nanopore.*

The operating voltage of an electrochemical capacitor is limited by the breakdown potential of the electrolyte (typically 1 to 3 V per cell) and is generally much lower than that of conventional electrostatic and electrolytic capacitors. In many practical applications, therefore, electrochemical capacitor cells must be series-connected, similar to batteries, to meet operating voltage requirements. To illustrate the major differences between secondary (rechargeable) batteries and electrochemical capacitors, important fundamental properties of each are compared in Table I. The fundamental difference between batteries and electrochemical capacitors is that the former store energy in the bulk of chemical reactants capable of generating charge, whereas the latter store energy directly as surface charge. Battery discharge rate and therefore power performance is then limited by the reaction kinetics as well as the mass transport, while such limitations do not apply to electrochemical capacitors constructed with two activated carbon electrodes, thereby allowing exceptionally high power capability during both discharge and charge. Most batteries exhibit a relatively constant operating voltage because of the thermodynamics of the battery reactants; as a consequence it is often difficult to measure their state-of-charge (SOC) precisely. On the other hand, for a capacitor, its operating voltage changes linearly with time during constant current operation so that the SOC can be exactly pinpointed. Furthermore, the highly reversible electrostatic charge storage mechanism in ECs does not lead to any volume change like observed in batteries with electrochemical transformations of active masses. This volume change limits the cyclability of batteries generally to several hundred cycles whereas ECs have demonstrated from hundreds of thousands to many millions of full charge/discharge cycles.

Electric double-layer capacitor

From Wikipedia, the free encyclopedia

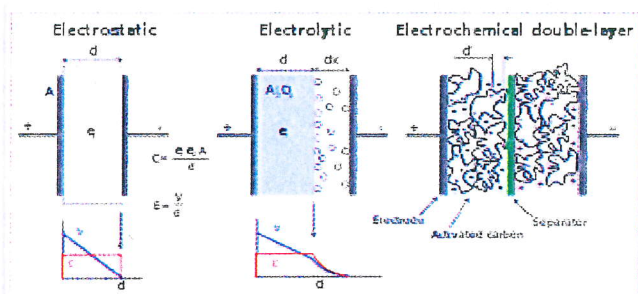
Maxwell Technologies "MC" and "BC" series supercapacitors (up to 3000 farad capacitance)

Electric double-layer capacitors, also known as **supercapacitors**, **electrochemical double layer capacitors (EDLCs)**, or **ultracapacitors**, are electrochemical capacitors that have an unusually high energy density when compared to common capacitors, typically on the order of thousands of times greater than a high capacity electrolytic capacitor. For instance, a typical D-cell sized electrolytic capacitor will have a capacitance in the range of tens of millifarads. The same size electric double-layer capacitor would have a capacitance of several farads, an improvement of about two or three orders of magnitude in capacitance, but usually at a lower working voltage. Larger, commercial electric double-layer capacitors have capacities as high as 5,000 farads.[1] The highest energy density in production is 30 Wh/kg.[2]

Electric double-layer capacitors have a variety of commercial applications, notably in "energy smoothing" and momentary-load devices. Some of the earliest uses were motor startup capacitors for large engines in tanks and submarines, and as the cost has fallen they have started to appear on diesel trucks and railroad locomotives.[3] More recently they have become a topic of some interest in the green energy world, where their ability to store energy quickly makes them particularly suitable for regenerative braking applications, whereas batteries have difficulty in this application due to slow charging rates. New technology in development could potentially make EDLCs with high enough energy density to be an attractive replacement for batteries in all-electric cars and plug-in hybrids, as EDLCs are quick charging and exhibit temperature stability. They can also be used in PC Cards, flash photography devices in digital cameras, portable media players, and in automated meter reading [4].

Concept

In a conventional capacitor, energy is stored by the removal of charge carriers, typically electrons, from one metal plate and depositing them on another. This charge separation creates a potential between the two plates, which can be harnessed in an external circuit. The total energy stored in this fashion is proportional to both the number of charges stored and the potential between the plates. The number of charges stored is essentially a function of size and the material properties of the plates, while the potential between the plates is limited by the dielectric breakdown. Different materials sandwiched between the plates to separate them result in different voltages to be stored. Optimizing the material leads to higher energy densities for any given size of capacitor.



Comparison of construction diagrams of three capacitors. Left: "normal" capacitor, middle: electrolytic, right: electric double-layer capacitor

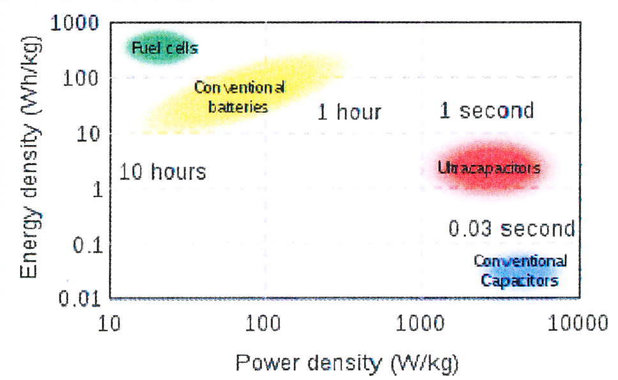
NOTE: The activated carbon granules are in electrical contact with each other to constitute a "plate" with a huge surface area. The separator is permeable to the electrolyte.

In contrast with traditional capacitors, electric double-layer capacitors do not have a conventional dielectric. Rather than two separate plates separated by an intervening substance, these capacitors use "plates" that are in fact two layers of the same substrate, and their electrical properties, the so-called "electrical double layer", result in the effective separation of charge despite the vanishingly thin (on the order of nanometers) physical separation of the layers. The lack of need for a bulky layer of dielectric permits the packing of "plates" with much larger surface area into a given size, resulting in their extraordinarily high capacitances in practical sized packages.

In an electrical double layer, each layer by itself is quite conductive, but the physics at the interface where the layers are effectively in contact means that no significant current can flow between the layers. However, the double layer can withstand only a low voltage, which means that electric double-layer capacitors rated for higher voltages must be made of matched series-connected individual electric double-layer capacitors, much like series-connected cells in higher-voltage batteries.

In general, electric double-layer capacitors improve storage density through the use of a nanoporous material, typically activated charcoal, in place of the conventional insulating barrier. Activated charcoal is a powder made up of extremely small and very "rough" particles, which in bulk form a low-density volume of particles with holes between them that resembles a sponge. The overall surface area of even a thin layer of such a material is many times greater than a traditional material like aluminum, allowing many more charge carriers (ions or radicals from the electrolyte) to be stored in any given volume. The downside is that the charcoal is taking the place of the improved insulators used in conventional devices, so in general electric double-layer capacitors use low potentials on the order of 2 to 3 V.

Activated charcoal is not the "perfect" material for this application. The charge carriers are actually (in effect) quite large - especially when surrounded by solvent molecules - and are often larger than the holes left in the charcoal, which are too small to accept them, limiting the storage. Recent research in electric double-layer capacitors has generally focused on improved materials that offer even higher *usable* surface areas. Experimental devices developed at MIT replace the charcoal with carbon nanotubes, which have similar charge storage capability as charcoal (which is almost pure carbon) but are mechanically arranged in a much more regular pattern that exposes a much greater suitable surface area.[5] Other teams are experimenting with custom materials made of activated polypyrrole, and even nanotube-impregnated papers.



Ragone chart showing energy density vs. power density for various energy-storage devices

In terms of energy density, existing commercial electric double-layer capacitors range around 0.5 to 30 W·h/kg, with the standardized cells available from Maxwell Technologies rated at 6 W·h/kg and ACT in production of 30 Wh/kg. [6][7] Note however that ACT's capacitor is actually a Lithium ion capacitor, known also as a "hybrid capacitor". Experimental electric double-layer capacitors from the MIT LEES project (http://lees.mit.edu/lees/ultracapacitors.htm) have demonstrated densities of 30 W·h/kg and appear to be scalable to 60 W·h/kg in the short term,[8] while EEStor claims their examples will offer capacities about 400 W·h/kg. For comparison, a conventional lead-acid battery is typically 30 to 40 W·h/kg and modern lithium-ion batteries are about 160 W·h/kg. Also, gasoline has a net calorific value (NCV) of around 12,000 W·h/kg, which in automobile applications operates at 20% tank-to-wheel efficiency giving an effective energy density of 2,400 W·h/kg.

Additionally, electric double-layer capacitors offer much higher power density than batteries. Power density combines the energy density with the speed that the energy can be drawn out of the device. Batteries, which are based on the movement of charge carriers in a liquid electrolyte, have relatively slow charge and discharge times. Capacitors, on the other hand, can be charged or discharged at a rate that is typically limited by current heating of the electrodes. So while existing electric double-layer capacitors have energy densities that are perhaps 1/10th that of a conventional battery, their power density is generally ten to one-hundred times as great (see diagram, right).

History

The electric double-layer capacitor effect was first noticed in 1957 by General Electric engineers experimenting with devices using porous carbon electrode.[9] It was believed that the energy was stored in the carbon pores and it exhibited "exceptionally high capacitance", although the mechanism was unknown at that time.

General Electric did not immediately follow up on this work, and the modern version of the devices were eventually developed by researchers at Standard Oil of Ohio in 1966, after they accidentally re-discovered the effect while working on experimental fuel cell designs.[10] Their cell design used two layers of activated charcoal separated by a thin porous insulator, and this basic mechanical design remains the basis of most electric double-layer capacitors to this day.

Standard Oil also failed to commercialize their invention, licensing the technology to NEC, who finally marketed the results as “supercapacitors” in 1978, to provide backup power for maintaining computer memory.[10] The market expanded slowly for a time, but starting around the mid-1990s various advances in materials science and simple development of the existing systems led to rapidly improving performance and an equally rapid reduction in cost.

The first trials of supercapacitors in industrial applications were carried out for supporting the energy supply to robots. [11]

In 2005 aerospace systems and controls company Diehl Luftfahrt Elektronik GmbH chose ultracapacitors Boostcap (of Maxwell Technologies) to power emergency actuation systems for doors and evacuation slides in passenger aircraft, including the new Airbus 380 jumbo jet. Also in 2005, the ultracapacitor market was between US $272 million and $400 million, depending on the source.

In 2006, Joel Schindall and his team at MIT began working on a "super battery", using nanotube technology to improve upon capacitors. They hope to put them on the market within five years.

Recently [12], all solid state micrometer-scale electric double-layer capacitors based on advanced superionic conductors have been for future low-voltage electronics such as deep-sub-voltage nanoelectronics and related technologies (the 22 nm technological node of CMOS and beyond).

Alternative energy sources

The idea of replacing batteries with capacitors in conjunction with novel alternative energy sources became a conceptual umbrella of the Green Electricity (GEL) Initiative [2] (http://www.alexanderbell.us/Initiative/GEL.htm) , [3] (http://www.alexanderbell.us/Project/GreenElectricity.htm) , introduced by Dr. Alexander Bell. One particular successful implementation of the GEL Initiative concept was a muscle-driven autonomous solution which employs a multi-farad electric double-layer capacitor (hecto- and kilofarad range capacitors are now available) as an intermediate energy storage to power a variety of portable electrical and electronic devices such as MP3 players, AM/FM radios, flashlights, cell phones, and emergency kits.[13] As the energy density of electric double-layer capacitors is bridging the gap with batteries, the vehicle industry is deploying ultracapacitors as a replacement for chemical batteries.

Technology

Supercapacitors has several disadvantages and advantages relative to batteries: [14]

Disadvantages

- The amount of energy stored per unit weight is considerably lower than that of an electrochemical battery (3-5 W.h/kg for an ultracapacitor compared to 30-40 W.h/kg for a battery). It is also only about 1/10,000th the volumetric energy density of gasoline.
- The voltage varies with the energy stored. To effectively store and recover energy requires sophisticated electronic control and switching equipment.
- Has the highest dielectric absorption of all types of capacitors.

Advantages

- Very high rates of charge and discharge.
- Little degradation over hundreds of thousands of cycles.
- Good reversibility
- Low toxicity of materials used.
- High cycle efficiency (95% or more)

Discharge cycles

Due to the capacitor's high number of charge-discharge cycles (millions or more compared to 200–1000 for most commercially available rechargeable batteries) there are no disposable parts during the whole operating life of the device, which makes the device environmentally friendly. Batteries wear out on the order of a few years, and their highly reactive chemical electrolytes present a serious disposal and safety hazard. This can be improved by only charging under favorable conditions, at an ideal rate, and, for some chemistries, as infrequently as possible. Electric double-layer capacitors can help in this regard, acting as a charge conditioner, storing energy from other sources for load balancing purposes and then using any excess energy to charge the batteries only at opportune times.

Low internal resistance

Other advantages of electric double-layer capacitors compared with rechargeable batteries are extremely low internal resistance or ESR, high efficiency (up to 97-98%), high output power, extremely low heating levels, and improved safety. According to ITS (Institute of Transportation Studies, Davis, CA) test results, the specific power of electric double-layer capacitors can exceed 6 kW/kg at 95% efficiency [15]

Materials

Activated Carbon, Graphene, carbon nanotubes and certain conductive polymers, or carbon aerogels, are practical for supercapacitors:

Virtually all commercial supercapacitors manufactured by Panasonic, Nesscap, Maxwell, Nippon Chemicon, Axion Power, and others use powdered activated carbon made from coconut shells. Some companies also build higher performance devices, at a significant cost increase, based on synthetic carbon precursors that are activated with potassium hydroxide (KOH).

- Graphene has excellent surface area per unit of gravimetric or volumetric densities, is highly conductive and can now be produced in various labs. It will not be long before large volumes of Graphene is produced for supercapacitors. For more details on this technology, refer to work of Prof. Rod Ruoff at the University of Texas.

- Carbon nanotubes have excellent nanoporosity properties, allowing tiny spaces for the polymer to sit in the tube and act as a dielectric. MIT's Laboratory of Electromagnetic and Electronic Systems (LEES) is researching using carbon nanotubes[16].

- Some polymers (eg. polyacenes) have a redox (reduction-oxidation) storage mechanism along with a high surface area.

- Supercapacitors are also being made of carbon aerogel. This is a unique material providing extremely high surface area of about 400-1000 m^2/g. The electrodes of aerogel supercapacitors are usually made of non-woven paper made from carbon fibers and coated with organic aerogel, which then undergoes pyrolysis. The paper is a composite material where the carbon fibers provide structural integrity and the aerogel provides the required large surface. Small aerogel supercapacitors are being used as backup electricity storage in microelectronics, but applications for electric vehicles are expected. The voltage of an aerogel capacitor is limited to a few volts. Higher voltages will lead to ionization of the carbon, which will damage the capacitor. Carbon aerogel capacitors have achieved 325 J/g (90 Wh/kg) energy density and 20 W/g power density.[17]

- The company Reticle (http://reticlecarbon.com) claims to be able to make supercapacitors from activated carbon in solid form. This substance they call consolidated amorphous carbon (CAC). It can have a surface area exceeding 2800 m^2/g and according to US patent 6787235 (http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=US6787235) may be cheaper to produce than aerogel carbon.

- Systematic pore size control showed by Y-Carbon[18] can be used to increase the energy density by more than 100% than what is commercially available.

- The company Tartu Technologies (http://www.skeletonnanolab.com) developed supercapacitors from mineral-based carbon. This nonactivated carbon is synthesised from the metal- or metalloid carbides, e.g. SiC, TiC, Al4C3, etc. as claimed in US patent 6602742 (http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=US6602742) and WO patent 2005118471 (http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=WO2005118471) . The synthesised nanostructured porous carbon, often called Carbide Derived Carbon (CDC), has a surface area of about 400 m^2/g to 2000 m^2/g with a specific capacitance of up to 100 F/mL (in organic electrolyte). They claim a supercapacitor with a volume of 135 mL and 200 g weight having 1.6 kF capacitance. The energy density is more than 47 kJ/L at 2.85 V and power density of over 20 W/g.[19]

In August 2007, a research team at RPI developed a paper battery with aligned carbon nanotubes, designed to function as both a lithium-ion battery and a supercapacitor (called *bacitor*), using an ionic liquid, essentially a liquid salt, as the electrolyte. The sheets can be rolled, twisted, folded, or cut into numerous shapes with no loss of integrity or efficiency, or stacked, like printer paper (or a Voltaic pile), to boost total output. Further, they can be made in a variety of sizes, from postage stamp to broadsheet. Their light weight and low cost make them attractive for portable electronics, aircraft, automobiles, and toys (such as model aircraft), while their ability to use electrolytes in blood make them potentially useful for medical devices such as pacemakers. In addition, they are biodegradable.[20]

Transportation applications

See also: Capa vehicle

China is experimenting with a new form of electric bus (capabus) that runs without powerlines using power stored in large onboard electric double-layer capacitors, which are quickly recharged whenever the bus is at any bus stop (under so-called **electric umbrellas**), and fully charged in the terminus. A few prototypes were being tested in Shanghai in early 2005. In 2006, two commercial bus routes began to use electric double-layer capacitor buses; one of them is route 11 in Shanghai. [21]

In 2001 and 2002, VAG, the public transport operator in Nuremberg, Germany tested an hybrid bus which uses a diesel-electric battery drive system with electric double-layer capacitors.[22]

Since 2003 Mannheim Stadtbahn in Mannheim, Germany has operated an LRV (light-rail vehicle) which uses electric double-layer capacitors to store braking energy.[23][24]

Other companies from the public transport manufacturing sector are developing electric double-layer capacitor technology: The Transportation Systems division of Siemens AG is developing a mobile energy storage based on double-layer capacitors called Sibac Energy Storage [25] and also Sitras SES, a stationary version integrated into the trackside power supply [26]. The company Cegelec is also developing an electric double-layer capacitor-based energy storage system[27].

Proton Power Systems has created the world's first triple hybrid Forklift Truck, which uses fuel cells and batteries as primary energy storage and electric double-layer capacitors to supplement this energy storage solution.[28]