Technology Brief 12
Supercapacitors

As shown in Section 5-2.1, the energy (in joules) stored in a capacitor is given by $w = \frac{1}{2}CV^2$, where C is the capacitance and V is the voltage across it. Why then do we not charge capacitors by applying a voltage across them and then use them instead of batteries in support of everyday gadgets and systems? To help answer this question, we refer the reader to **Fig. TF12-1**, whose axes represent two critical attributes of storage devices. It is the combination (intersection) of these attributes that determines the type of applications best suited for each of the various energy devices displayed in the figure.

Energy density W' is a measure of how much energy a device or material can store per unit weight. That is, $W' = w/m$, where m is the mass of the capacitor in kilograms. [Alternatively, energy density can be defined in terms of volume (instead of weight) for applications where minimizing the volume of the energy source is more important than minimizing its weight.] Even though the formal SI unit for energy density is (J/kg), a more common unit is the watt-hour/kg (Wh/kg) with 1 Wh = 3600 J. The second dimension in **Fig. TF12-1** is the ***power density*** P' (W/kg), which is a measure of how fast energy can be added to or removed from an energy-storage device (also per unit weight). Power is defined as energy per unit time as $P' = dW'/dt$.

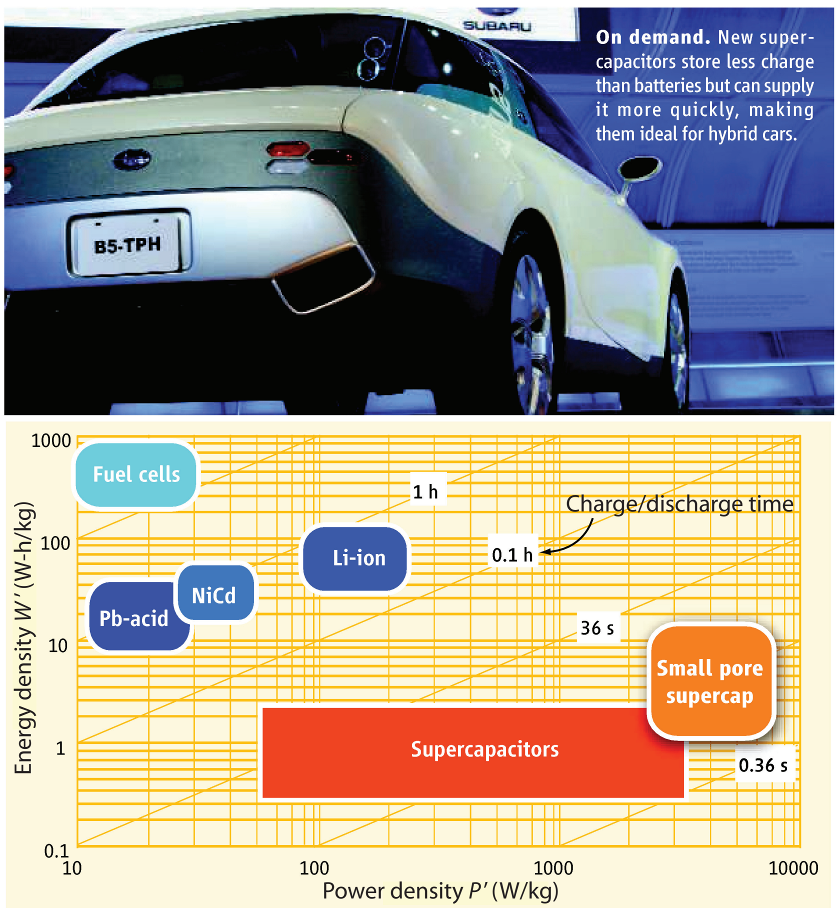


Figure TF12-1: Energy and power densities of modern energy-storage technologies. Even though supercapacitors store less charge than batteries, they can discharge their energy more quickly, making them more suitable for hybrid cars. (*Science*, Vol. 313, p. 902.)

Table TT12-1: Comparison of a conventional capacitor, supercapacitor, and lithium battery size and mass required to hold ~ 1 megajoule (MJ) of energy (300 watt-hours). 1 MJ of energy will power a laptop with an average consumption of 50 W for 6 hours. Note from the first column that a lithium ion battery might hold 1000 times more energy than a conventional capacitor for reasonable voltages (< 50 V).

Sample device	Specific Energy [Watt hours/ kg]	Specific Energy [MJ / kg]	Energy Density [MJ / liter]	Volume required to hold 1 MJ [liter]	Weight required to hold 1 MJ [kg]
Conventional capacitor	0.01 – 0.1	$4\text{x}10^{-5}$-$4\text{x}10^{-4}$	$6\text{x}10^{-5}$-$6\text{x}10^{-4}$	17000-1700	25000 - 2500
Supercapacitor	1 - 10	0.004 – 0.04	0.006 - 0.06	166 – 16	250 – 25
Lithium ion battery	100 - 250	0.36 - 0.9	1 - 2	1 – 0.5	2.8 – 1.1

According to **Fig. TF12-1**, fuel cells can store large amounts of energy, but they can deliver that energy only relatively slowly (several hours). In contrast, conventional capacitors can store only small amounts of energy—several orders of magnitude less than fuel cells—but it is possible to charge or discharge a capacitor in just a few seconds—or even a fraction of a second. Batteries occupy the region in-between fuel cells and conventional capacitors; they can store more energy per unit weight than the ordinary capacitor by about three orders of magnitude, and they can release their energy faster than fuel cells by about a factor of 10. Thus, capacitors are partly superior to other energy devices because they can accomodate very fast rates of energy transfer, but the amount of energy that can be "packed into" a capacitor is limited by its size and weight. To appreciate what that means, let us examine the relation

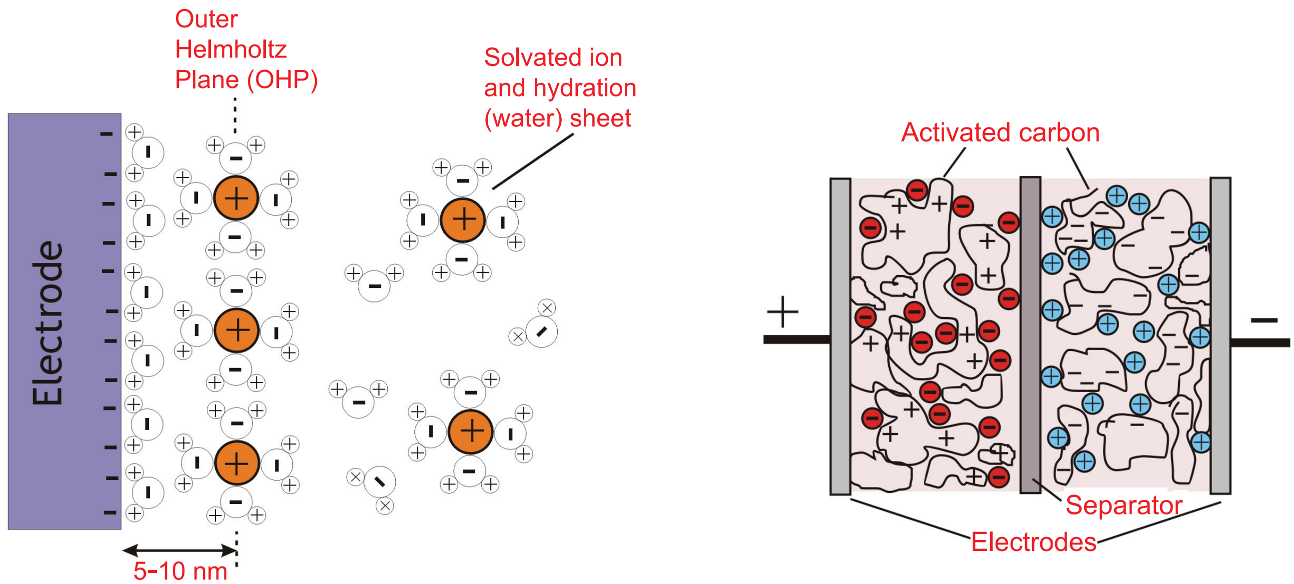
$$w = \frac{1}{2} CV^2.$$

To increase w, we need to increase either C or V. We can develop an intuitive feel for this if we compare how large a storage element would have to be to hold 1 MJ (~ 300 watt-hours). From **Table TT12-1**, we can see that a conventional capacitor would have to be thousands of liters in size (and weigh thousands of kilograms), whereas a supercapacitor or a battery would be considerably smaller.

For a parallel-plate capacitor, $C = \varepsilon A/d$, where ε is the permittivity of the material between the plates, A is the area of each of the two plates, and d is the separation between them. The material between the plates should be a good insulator, and for most such insulators, the value of ε is in the range between ε_0 (permittivity of vacuum) and $6\varepsilon_0$ (for mica), so the choice of material can at best increase C by a factor of 6. Making A larger increases both the volume and weight of the capacitor. In fact, since the mass m of the plates is proportional directly to A, the energy density $W' = w/m$ is independent of A. That leaves d as the only remaining variable. Reducing d will indeed increase C, but such a course will run into two serious obstacles: (a) to avoid voltage breakdown (arcing), V has to be reduced along with d such that V/d remains lower than the breakdown value of the insulator; (b) eventually d approaches subatomic dimensions, making it infeasible to construct such a capacitor. Increasing V also increases the energy stored (by V^2) but here, too, we run into problems with breakdown. Another serious limitation of the capacitor as an energy storage device is that its voltage does not remain constant as energy is transferred to and from it.

Supercapacitor Technology

A new generation of capacitor technologies, termed ***supercapacitors*** or ***ultracapacitors***, is narrowing the gap between capacitors and batteries. These capacitors can have sufficiently high energy densities to approach within 10 percent of battery storage densities, and additional improvements may increase this even more. Importantly, supercapacitors can absorb or release energy much faster than a chemical battery of identical volume. This helps immensely during recharging. Moreover, most batteries can be recharged only a few hundred times before they are degraded completely; supercapacitors can be charged and discharged millions



(a) (b)

Figure TF12-2: (a) Conceptual illustration of the water double layer at a charged metal surface; (b) conceptual illustration of an electrochemical capacitor.

of times before they wear out. Supercapacitors also have a much smaller environmental footprint than conventional chemical batteries, making them particularly attractive for green energy solutions.

History and Design

Supercapacitors are a special class of capacitor known as an ***electrochemical capacitor***. This should not be confused with the term ***electrolytic capacitor***, which is a term applied to a specific variety of the conventional capacitor. Electrochemical capacitors work by making use of a special property of water solutions (and some polymers and gels). When a metal electrode is immersed in water and a potential is applied, the water molecules (and any dissolved ions) immediately align themselves to the charges present at the surface of the metal electrode, as illustrated in **Fig. TF12-2(a)**. This rearrangement generates a thin layer of organized water molecules (and ions), called a ***double layer***, that extends over the entire surface of the metal. The very high charge density, separated by a tiny distance on the order of a few nanometers, effectively looks like a capacitor (and a very large one: capacitive densities on the order of $\sim 10\ \mu\text{F/cm}^2$ are common for water solutions). This phenomenon has been known to physicists and chemists since the work of von Helmholtz in 1853, and later Guoy, Chapman, and Stern in the early 20th century. In order to make capacitors useful for commercial applications, several technological innovations were required. Principal among these were various methods for increasing the total surface area that forms the double layer. The first working capacitor based on the electrochemical double layer (patented by General Electric in 1957) used very porous conductive carbon. Modern electrochemical capacitors employ ***carbon aerogels***, and more recently ***carbon nanotubes*** have been shown to effectively increase the total double layer area (**Fig. TF12-2(b)**).

Supercapacitors are beginning to see commercial use in applications ranging from transportation to low-power consumer electronics. Several bus lines around the world now run with buses powered with supercapacitors; train systems are also in development. Supercapacitors intended for small portable electronics (like your MP3 player) are in the pipeline as well!