



POWER ELECTRONICS SOCIETY NEWSLETTER

First Quarter 2008
Volume 20, Number 1
ISSN 1054-7231

President's Message

INTELEC® Fellowship

IEEE Medal Award

Fellow Nomination Process

PEL's 2008 Fellows



What's in a Name?

A New Model for Regenerative Electrical Energy Storage

Joel Schindall,
Member, IEEE

Bernard Gordon Professor of Product Design, EECS Department, MIT

A tale of batteries, capacitors, and... batacitors?

Sometimes we can gain great insight into a device by thinking a bit about the concept of operation. Batteries have been around for so long (since the Volta Pile in 1800) that no one reflects much on their basic principle of operation. Most people would define a battery as “a chemical way to store electrical energy.” If asked for more detail, they would focus on the chemical interactions that take place in the electrodes of the battery.

Perhaps this is misleading. I would submit that the real phenomenon that is taking place in a battery is that ions, i.e. electrical charges, are migrating from one electrode or plate into the electrolyte and a corresponding number of ions from the electrolyte are being stored through a redox combination in the other. The resulting electrochemical potential is what produces the voltage, but it is the ion transfer and storage that supports the charge storage and hence the current. For any given electrochemical potential, the energy storage capability is directly proportional to the number of ions that can be absorbed in the electrodes.

A capacitor stores electrical energy in quite a different manner. There is no electrolyte and there is no ion flow. The voltage is generated by an electrical field rather than an electrochemical potential, and the current results from electron accumulation/depletion in the electrodes rather than ion transfer.

There is a less-well-known device commonly referred to as an ultracapacitor, double-layer capacitor (DLC), electrochemical capacitor, or supercapacitor, which falls between a battery and a capacitor. In fact, I would suggest that the abundance of names suggests an ambivalence about whether its fundamental physics are those of a battery or that of a capacitor. An ultracapacitor consists of two inert porous electrodes (usually aluminum coated with a thin layer of activated carbon) separated by a porous insulator and filled with an electrolyte similar to that used in a battery (figure 1). When a voltage is applied to the electrodes, ions from the electrolyte are attracted to and stored in the pores of the plate with opposite charge. There is no chemical reaction, but a capacitive voltage builds up between the ion layer and the porous carbon. So the voltage is generated capacitively by the electrical field between the ion layer and the carbon, but the current results from battery-like ion transfer and storage in the plates. An ultracapacitor can achieve a capacitance $C = \frac{A}{d}$ that is over ten million times higher than an equivalent metal-plate capacitor, simply because the effective surface area “A” of the activated carbon is tens of thousands greater than the linear surface area, and the effective spacing “d” between the ions and the carbon is more than a thousand times smaller than the spacing between the plates of the device. To give a specific example, commercial ultracapacitors the size of a D-cell battery are typically rated at 350 farads, while a paper capacitor the same size would be more like 20 microfarads.

I would suggest that both the ultracapacitor and the battery are fundamentally ion storage devices. The amount of charge they can store is equal to the ion storage (absorption) capability of the electrodes. The battery stores these ions via an electrochemical redox-couple reaction (Faradaic reaction), and generates its voltage through the electrochemical potential defined in the periodic table, whereas the ultracapacitor stores the ions electrostatically (non-

Faradaic) without a chemical reaction and generates its voltage through the Helmholtz capacitance that is formed at the interstitial layer. However, the voltages obtained in both devices are similar, so the energy storage capacity is basically proportional to the number of ions that can be stored (absorbed).

To review, there are three primary differences between the battery and the ultracapacitor:

1. The battery electrochemically reacts the ions either volumetrically within a chemical lattice (e.g. Li-Ion) or via surface plating (e.g. lead-acid), whereas the ultracapacitor electrostatically stores the ions fractally within a highly porous material, i.e. the storage “volume” is dependent on the surface area of the highly convoluted or “fractal” structure of the activated carbon or other porous electrode material [thanks to John Miller of Maxwell for suggesting the analogy to fractal geometry].
2. The battery generates its voltage chemically, while the ultracapacitor develops its voltage capacitively.
3. The battery derives its ions from the electrode material, while the ions stored in the plates of a charged ultracapacitor are derived from the ions present in the electrolyte solution.

I suggest that items 2 and 3 do not represent significant differences. Regarding item 2, the voltages are in a similar range and the charge dependence of the capacitor voltage is easily regulated by external circuitry. In fact, the overwhelming advantage here rests with the ultracapacitor. Because there is no chemical reaction, an ultracapacitor typically achieves efficiencies in the high 90% range and can be charged and discharged in just a few seconds. Also, lack of a chemical reaction means almost unlimited lifetime (both shelf life and charge-discharge cycles) and limited degradation at low temperatures. Regarding item 3, this means that ultracapacitors require sufficient electrolyte ions (molarity) to support the total amount of stored energy. This represents somewhat of a limit, but electrolytes in the 2 molar concentration range that are available today can support up to 80 Wh/kg, and higher molarity electrolytes are a promising research area.

So the primary issue is item 1: *how many ions can be stored in the electrode per unit weight or volume*. The primary limitation of today's commercial ultracapacitors is that they can generally store only about 5% as many ions as a modern Li-Ion battery. So for most applications, their long lifetime and rapid charge/discharge characteristics are not enough to overcome their limited storage capacity.

The key issue here seems to be that a chemical lattice structure such as that of a Li-Ion battery is a very volumetrically-efficient way to store ions. Activated carbon is extremely porous, but its fractal surface area is simply not as great (and the irregularities of the pore sizes further reduce its effectiveness). If we could find an inert, conductive electrode material with sufficiently high (fractal) surface area, I submit that we could increase the energy storage capacity of ultracapacitors to the point where it approximates that of batteries. Since ultracapacitors are superior to batteries in almost every regard other than total energy (e.g. charge/discharge rate, lifetime, cold temperature performance), this would be a profound breakthrough. (As mentioned: ultracapacitor voltage is charge-dependent, but this is easily overcome with external charge pumps. Also, the ion depletion in the electrolyte is an issue, but this might be overcome with higher molarity electrolytes or the use of ionic liquids.)

Nanotechnology to the rescue

We have seen that activated carbon has an immense interior surface area, but it still falls short of the volumetric ion storage efficiency of a chemical battery electrode. What if we could nano-engineer an inert electrode structure whose porosity allows it to have as much “internal volume” for electrolyte ions as the chemical lattice of, say, a lithium ion battery? In a way, we are talking of engineering a fractal surface whose surface area permits as much volumetric ion absorption as the three-dimensional lattice of a traditional battery electrode compound. There seems to be no physical reason that this cannot be done. The key question is what natural phenomenon might accomplish this (because we are constrained to operate within the natural scaffolding of Nature’s materials), and how to find and implement a realistic and cost-effective process for producing this material.

One such approach (and this is only one of many possibilities) is some work being carried on in my group in the Laboratory for Electromagnetic and Electronic Systems at the Massachusetts Institute of Technology. Many researchers have demonstrated that a microscopic forest of vertically aligned nanotubes can be grown on a (nonconductive) silica substrate by use of a thin catalyst layer and a chemical vapor deposition process. The silica is coated by a nanometer-thick layer of a catalyst such as iron. When the material is heated in a vacuum, the catalyst breaks into tiny droplets. When a hydrocarbon gas is passed over the substrate, carbon atoms are grabbed by the catalyst and a long nanotube self-assembles and pushes upward from the catalyst droplet.

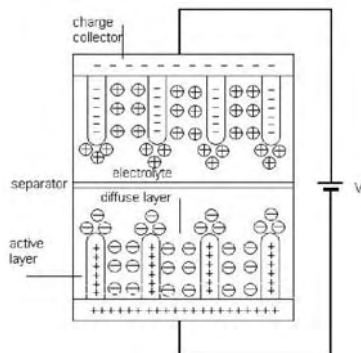


Fig. 1 Diagram of Nanotube-Enhanced Ultracapacitor Configuration (not to scale – nanotubes are much longer than shown) Top and bottom ends are the electrodes. Vertical tubes are the nanotubes. Circles are the ions. + and – signs represent positive and negative charges

Our work is still in process, but we have demonstrated that nanotube forests can also be grown on a conductive substrate. As compared to activated carbon, this is somewhat analogous to a paintbrush as opposed to a sponge. Our calculations indicate that the surface area of this forest should exceed the effective surface area of activated carbon devices by at least a factor of five, and we also anticipate being able to operate at higher voltages due to the inert chemistry of the nanotubes as compared to activated carbon. In our early testing we have measured true ultracapacitor action with extremely low impedance, but the cell chemistry is complex and we have not yet refined our cell assembly to the point of verifying the anticipated energy density increase.

How we model the world defines what we can do with it!

We certainly hope for success with our nanotube forest, but the primary point of this article is to suggest that viewing the battery as pri-

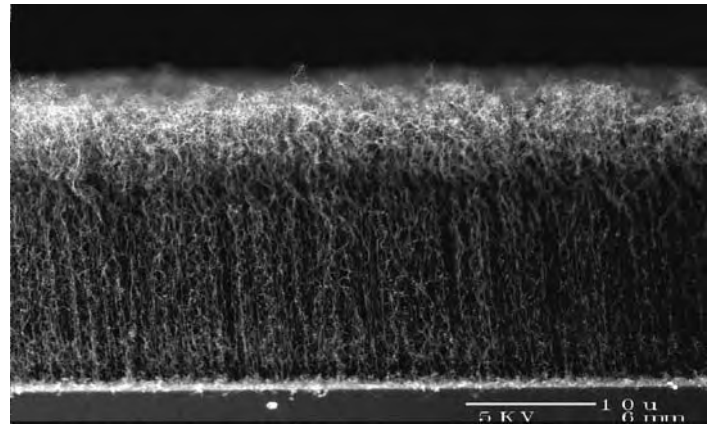


Fig. 2 Electrode cross-section. Bottom plate is the electrode, vertical “hairs” are the nanotubes (courtesy, Riccardo Signorelli, research assistant, MIT Laboratory for Electromagnetic and Electronic Systems).

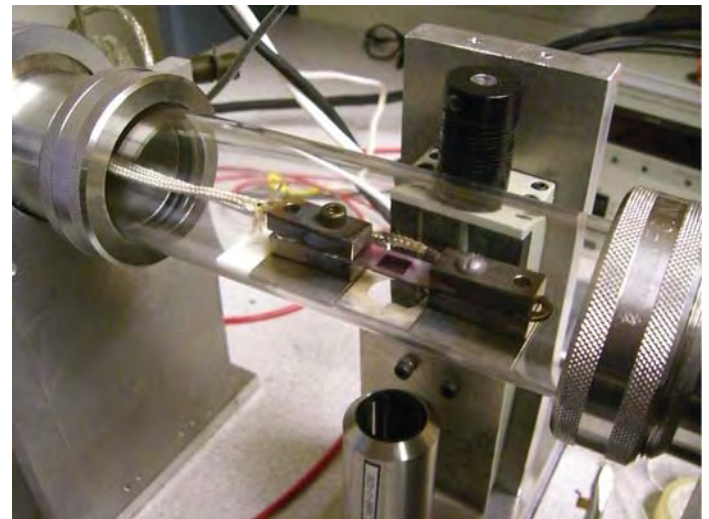


Fig. 3 Chemical Vapor Deposition (CVD) growth chamber with carbon nanotube sample in place

marily an ion storage devices leads to the insight that perhaps the storage mechanism itself does not have to be chemical. To some, a non-chemical battery may seem like a contradiction in terms (though I would point out that the term “battery” was coined by Benjamin Franklin to describe a stack of charged glass plates which we would now call – a capacitor). Almost everything that is “bad” about batteries (relatively short lifetime, limited high current capability and poor low temperature capability) stems from the chemical reactions in the electrodes. In the 1960s, Philip Jose Farmer launched the science fiction series “Riverworld” in which huge ships are powered by a wondrous rechargeable device called a batacitor. We now have the technology to engineer a wide variety of passive electrode structures with high accessibility and fractal-like surface area. Perhaps it is time to use this technology to re-invent the battery.



Joel Schindall received his BS, MS and PhD in electrical engineering from MIT in the 1960's. After a 35 year technical and management career in the aerospace, telecommunications, and satellite industries, including president of Loral Conic and Chief Engineer of Globalstar, he returned to MIT in 2002 as the Bernard Gordon Professor of Product Design in the Electrical Engineering and Computer Science Department.