THE NON-BATTERY BATTERY - THE POTENTIAL ROLE OF SUPERCAPACITORS IN STANDBY POWER APPLICATIONS.

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INTRODUCTION

In the 140 years since Gaston Plante demonstrated the first lead-acid battery there has been nothing yet to rival the rechargeable battery in all its forms – through nickel-cadmium and nickel-metal-hydride to the latest high-tech Lithium-Ion chemistries -as a method of storing electrical energy for later usage. That is what batteries are particularly good at. It's getting the electrical energy out of a battery fast enough that can sometimes create difficulties.

At relatively low rates of discharge, say five hours, a battery can be totally discharged and 100 percent of the stored energy can be obtained. However, at very high rates of discharge, say just a few seconds, only a few percent of the stored capacity is used for the discharge. So, although the battery can perform the duty, and regularly does, it requires an electrical capacity, and therefore weight and volume, which is much higher than the electrical output required. Lead-acid batteries have the additional problem that, when optimised for high-rate discharges (as in automotive batteries), their operating life in industrial applications is very short.

Capacitors exist at the opposite end of the scale. They store power as static electricity rather than in the reversible, faradaic chemical reaction found in a battery. And they can deliver all their stored energy virtually instantaneously – within a few thousandths of a second. But the amount available is actually tiny, just enough to pop a flashbulb.

Now, with the recent emergence of supercapacitors, there seem to be the possibility of an ideal compromise, which combines some of the storage capabilities of batteries and some of the power discharge characteristics of capacitors in a device capable of storing useful quantities of electricity which can be discharged very quickly.

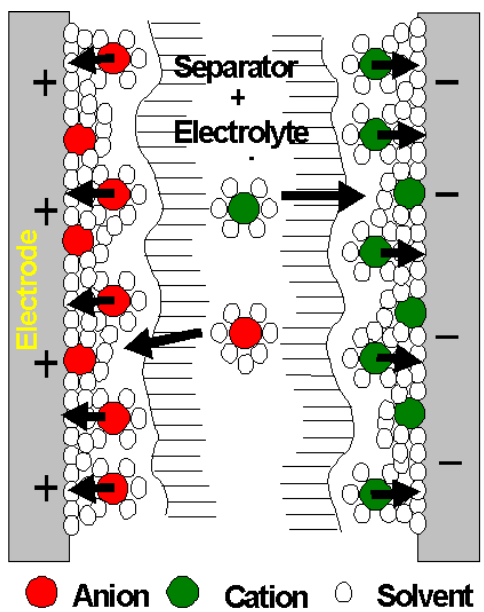
CLASSIC CAPACITORS

To understand exactly why supercapacitors are so special it is useful to consider the classic capacitor, a device for storing electric charge, which actually dates right back to the 'Leyden Jar' of the mid-eighteenth century. At its simplest, a capacitor is constructed by taking two metal plates and sandwiching them close together with an insulator (a vacuum, paper or other insulating material) in between them and then connecting one plate to the positive pole of a power source and the other to the negative pole.

The greater the surface area of the plates and the closer that they are brought together then the higher the charge storing capability, or 'capacitance' of the capacitor. Capacitance is measured in Farads (F) – a 1 F capacitor charged to 1 V can supply 1 A of current for 1 second. Typical modern capacitors usually feature a rolled construction using a metallised plastic film to store the charge, even so the highest value capacitors available do not even approach one Farad and are actually measured in microfarads, which of course is all that is required for most electronic applications.

The use of capacitors as practical energy storage devices only became possible with the emergence over the past 20 years of supercapacitors, which are sometimes also known as 'ultracapacitors' – the terms are interchangeable. In contrast to ordinary capacitors their capacitance is measured in whole Farads (F), and now even kiloFarads (kF), which means that they can store million times the electrical charge.

SUPERCAPACITOR TYPES



The first type of supercapacitor replaces the flat metal sheets with activated carbon electrodes. The microscopic pores in the carbon (typically just a few nanometres in size) have the effect of providing an enormously increased internal surface area, greater than 1000 square metres per gramme. In order to utilise this additional active surface area it is necessary to use an electrically conductive liquid electrolyte. It is important to remember that the two electrodes are not directly analogous to the two plates of a conventional capacitor. Instead, on each of the electrodes an electrical double layer of charge is formed between the carbon and the electrolyte ions. In effect, you have a complete capacitor at each electrode, which makes the complete device two capacitors connected in series, and a supercapacitor based on this principle is sometimes referred to as an electrochemical double-layer (EDL) capacitor.

A variety of electrolytes can be used in supercapacitors, including water-based solutions such as potassium hydroxide or sulphuric acid. However, since water tends to break down into hydrogen and oxygen at voltages over 1 V, these supercapacitors can only be used up to 1 V. But if a water free organic solvent is utilised for the electrolyte then we can create a supercapacitor useable up to 2.5 V or higher.

The second type of supercapacitor uses transition metal oxides (ruthenium or iridium) as electrode material with an aqueous electrolyte. In that case, the operating mode is not exclusively electrostatic but relies mainly on highly reversible surface faradaic reactions[1,2].

The third type of supercapacitor is based on the use of electronic conducting polymers such as polypyrrole, polythiophene or polyaniline [3]. These polymers go from the insulating state to the conducting state by anion doping (p-doping process). The first step corresponds to a faradaic process characterised by a standard potential. Anions can be added in a second step by overdoping without any change in the conducting properties. The amount of injected charge is proportional to the applied voltage (capacitive behaviour).

SAFT SUPERCAPACITORS

Considering the technical maturity, the manufacturing processes, the expected performances and costs, activated carbon based supercapacitors are the most interesting and promising devices for industrial applications. This is the approach we have taken in the design of Saft's own range of supercapacitors, manufactured in a new facility in Bordeaux, France (see table 1 for specification).

Table 1 Supercapacitor Specification

Rated Capacitance	3500 F
Nominal voltage Maximum voltage Minimum voltage	2.5 Volts 2.7 Volts 0 Volts (1.0 Volts for practical purposes)
Resistance HFR ESR	< 0.5 mΩ (1 kHz or 2s pulse) < 1 mΩ (0.01 Hz)
Dimensions (diameter * height)	55 * 220 mm
Volume	0.5 l
Weight	0.65 kg
Maximum Current	1000 A (750 A repetitive)
Maximum specific power	3225 W/kg at 500 A
Operating temperature range	-40 °C to +60 °C
Transport and storage temperature	-40 °C to +70 °C

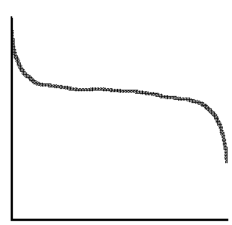
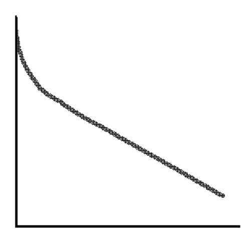
The manufacture of the Saft supercapacitors draws upon many of the production techniques already developed for Lithium-Ion rechargeable batteries, including the use of electrodes manufactured using carbon powder and a classical ink coating process in a spiral wound configuration and housed in an aluminium container. In order to achieve the target capacitance of 3500 F two seven metre long electrodes with an activated carbon loading of 5 milligrammes per square centimetre are employed, these are calendared down to a thickness of 100 micrometres and 70 percent porosity. A high conductivity organic electrolyte is also used.

SUPERCAPACITOR PERFORMANCE

The reason for the interest in supercapacitors soon becomes apparent from the table, which compares their performance with accumulators.

When considering the Specific Energy/Energy Density, which relates energy storage capacity in relation to weight (Wh/kg) we find that even though the extremely high capacitance of supercapacitors enables them to store a useable amount of energy, this is still only around one twelfth of what could be stored in a typical lead-acid battery and nearly thirty times less than a Lithium-ion battery (5 Wh/kg for supercapacitor and 140 Wh/kg for li-ion). But when we consider Specific Power/Power Density (in kW/kg), which measures how fast a supercapacitor or battery can

Table 2 Comparison between Accumulators and Supercapacitors

	Accumulators	**Supercapacitors**
Energy Storage Method	**Faradic reactions** Mass transfer between the electrodes	**Mostly electrostatic interactions** Ionic charge accumulation at the active material/electrolyte interface
Discharge Curve		
Cycle Life	**Depending on cycling profile** Impact of the active material degradation and parasitic phenomena such as electrolyte degradation.	**>> 1 000 000 (100% DOD)** Impact of parasitic phenomena such as electrolyte degradation.
Energy Level	**60 Wh/kg (alkaline)** **140 Wh/kg (Li-ion)**	**1-10 Wh/Kg**
Power Level	**0.4-0.8 kW/kg (alkaline)** **0.3-01.5 kW/kg (Li-ion)**	**1-6 kW/kg**

deliver its energy in relation to its weight and volume, then we see that the supercapacitor can vastly outperform virtually any battery.

Another important advantage of supercapacitors is their longevity and low temperature dependence. Since a battery depends on a chemical reaction between its electrolyte and electrodes each charge-discharge cycle will cause both the active materials and the electrolyte to deteriorate, which means that its useful lifetime, when the full battery capacity is employed, is normally measured in hundreds or thousands of cycles (although Ni-MH or Li-ion batteries can achieve several hundred thousand cycles when used at a depth of discharge of just a few percent of capacity). During their lifetime some batteries, such as vented lead-acid and nickel-cadmium, will also require routine maintenance to top up the electrolyte.

In contrast, a carbon type supercapacitor is in theory a pure electrostatic device that stores energy with no physical changes taking place, which means that we might expect it to last forever! In practice, in the same way that chemical batteries consume water over time due to electrolysis of the solvent, the same process can occur with the supercapacitor's organic electrolyte, albeit to a much smaller degree. In addition, over a long period of time there will be some limitations linked to side reactions. Even so, if designed and used correctly we can reasonably expect a supercapacitor to achieve a typical life of several million cycles, with no maintenance required.

Temperature effects

Since the rate of the chemical reactions taking place in a battery are temperature dependent then a battery's performance will deteriorate at extremes of temperature. For example, a lead-acid battery can be expected to lose approximately one percent of its capacity and cranking power for every degree Celsius drop in temperature. Again, since there are no complicated chemical reactions taking place in a supercapacitor during normal operation and combined with the choice of a highly conductive organic electrolyte, its performance remains completely unaffected over a very wide range of temperatures from +70°C down to –20°C. Below this temperature the conductivity of the organic electrolyte will start to limit the performance of the supercapacitor. But even at –40°C half the power is still available.

Supercapacitor coupling

Individual supercapacitors can be coupled together to provide a unit with a required voltage in exactly the same way that electrochemical cells are assembled in series to create a battery. But this does have an important effect on the total capacitance of the unit. So if say five 2.5 V supercapacitors are connected in series to create a nominal 12.5 V unit then the capacitance of the assembly actually becomes one fifth of the original capacitance of a single supercapacitor. Power and energy, on the other hand, are additive in the same way that they are with conventional batteries.

APPLICATIONS

Not surprisingly, supercapacitors found their first application in military projects, such as starting diesel engines in battle tanks or submarines, or replacing batteries on board missiles. But they are now starting to find their way into many civil applications requiring a lightweight, maintenance-free, source of energy where the major need is a high peak discharge for less than 30 seconds. This includes engine starting, switch tripping, power quality and UPS systems where supercapacitors can provide the emergency power for the vital time needed to maintain an electrical supply network until the back-up generator comes on line.

At Saft we believe that one of the potentially most interesting areas of application for supercapacitors is when they are used in combination with other energy storage devices such as batteries or fuel cells. This 'hybrid' format enables a designer to effectively enjoy the 'best of both worlds' by combining a high energy density power source with the high power density of a supercapacitor.

To see how this works in practice imagine a supercapacitor connected in parallel with a battery so that it can meet the power requirements of an expected power surge – starting a car engine or fire pump or rapidly accelerating an electric vehicle. When the power surge is over then the supercapacitor will automatically be recharged by the battery so that it is ready for the next power surge. This ensures that the battery does not have to be over-dimensioned in order to meet a high power demand, while the supercapacitor does not need to store large amounts of energy. A simple parallel connection is the easiest to arrange for trial purposes but, depending on the specific application, it might not always be the most efficient.

The hybrid concept - practical test results

Saft has carried out some performance tests on a hybrid concept. In this case a five cell, 6 V nickel-metal hydride (NiMH) battery with a 22 Ah capacity was connected in parallel with three capacitors. It was subjected to a typical duty cycle for engine starting of a 15 second discharge at 350 A, followed by a 30 second rest during which the supercapacitors recharged from the battery.

The system was cycled until there was no energy left in the battery and we found that while the battery alone could achieve just seven starting cycles, the hybrid could achieve 14 discharges without recharge, at a higher average voltage. The original tests were carried out at 20°C and it was interesting to note that when the temperature was dropped to 0°C the battery could not sustain a single cycle, while the hybrid remained completely unaffected.

The indications are that this hybrid approach will become even more interesting for applications where the temperature is lower and/or the current pulses are shorter and where more resistive batteries such as lead-acid or nickel-cadmium are used. The particular advantage for the designer is that this type of supercapacitor/battery combination could offer the same (or even better performance) as a battery in a compact package less than a quarter of the weight.

In addition to engine starting applications, the combination battery/supercapacitor approach is already being utilised to good effect in the new breed of hybrid petrol engine/electric powered vehicles where the supercapacitor provides extra ‘punch’ for acceleration. As further developments in electric vehicles continue supercapacitors will significantly improve their duration by providing better recovery of energy recovered during regenerative braking.

Power quality applications

Another important area where supercapacitors are expected to make a significant impact is in the realm of the power quality of the electric supply. This has been a factor ever since the conception of electricity, but only over the last two decades, due to the advances in technology, has it become a serious problem. The widespread use of computers in the 1980s and the network revolution in the 1990s brought the potential for more interference and created many new problems. This has lead to a requirement for the utilities to produce a 'clean' electrical supply free from surges and harmonics.

The supercapacitor is easily able to provide the few seconds or milli-seconds of discharge required to smooth out these aberrations. And, coupled with its 'fit and forget' maintenance-free nature, it has the potential to be the ideal product for power quality applications.

SUMMARY

To summarise the benefits of supercapacitors over conventional batteries:

- they can provide high discharge currents, up to 1000A, not easily achieved by batteries
- the recharge rate is rapid (as fast as discharge)
- they are highly efficient (up to 93% energy efficiency for a complete charge/discharge cycle)
- they can be charged and discharged almost indefinitely and have a long service life
- they require no maintenance and are ideal for use in remote locations
- supercapacitor/battery hybrids can achieve major improvements in battery performance at around a quarter of the weight

REFERENCES

1. B.E. Conway, *J. Electrochem. Soc.*, 138, (1991), 1539.
2. A.F. Burke, M. Miller and J.T. Guerin, *Recent Test Results for Aqueous and Organic Electrolyte Ultracapacitors*, Sixth International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Florida, USA, dec. 1996, and references therein.
3. A. Rudge, J. Davey, I. Raistrick and S. Gottesfeld, *Conducting Polymers as Potential active materials in electrochemical supercapacitors*, Second International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Florida, USA, dec. 1992, and references therein.