Abstract

The superior power of supercapacitors including asymmetric nickel carbon capacitors has long been recognized. The main advantage of this technology is its ability to quickly accumulate and deliver high power even at low temperatures. Asymmetric nickel capacitors, in particular, offer even better energy storage capabilities compared to its symmetric counterpart and are safer due to the use of aqueous electrolyte. These types of supercapacitors are proving to be viable cost-effective solutions for a variety of applications including heavy duty diesel engine starting, emergency power systems, and storing kinetic energy among others.

Introduction

Our need for energy storage devices which can both store energy as well as deliver substantial power is constantly increasing. Typically, batteries are the preferred energy storage solution for the majority of applications. As of today, Li-ion is the most popular technology due to its very high energy and power density. Amongst the other types of energy storage technologies, capacitors are also well positioned for applications requiring very high-power.
Overview of capacitor technology

Capacitors generally function by storing energy through the distribution of charge on an electrode surface. A traditional electrostatic capacitor stores the charge on conductive plates separated by an insulating medium as shown in Figure 1. As there is no chemical reaction taking place, a capacitor can charge and discharge very quickly with little resistance i.e. they have a very large power capability.¹

![Figure 1 A schematic demonstrating a charged versus a discharged parallel-plate capacitor](image)

The capacitance is given by the equation:

$$C = \frac{\varepsilon A}{d}$$

Where, $C$ is the capacitance, $A$ is the Area of the conducting plate surface, $d$ is the distance between the plates and $\varepsilon$ is the permittivity of the material.
From this equation we can see that the capacitance can be enhanced both by increasing the surface area and decreasing the distance between the plates. This is the principle behind “supercapacitors”; they take advantage of this storage mechanism by utilizing materials that have a very large surface area. The ions in the electrolyte distribute only nanometers from the surface of the electrode when charged creating a “double layer” that has only nanometers of distance between each layer. Going back to equation 1 we see that with a large surface area and a small distance between the layers it is possible to obtain phenomenal capacitances. Moreover, it is still capable to operate extremely fast and to deliver a significant amount of energy.

Figure 2  A schematic demonstrating the internal cell structure of a standard symmetric supercapacitor and a Saft asymmetric Nickel capacitor
Supercapacitors therefore represent alternative devices for energy and power storage, especially for applications for which the energy is required for only a relatively short time-frame e.g. engine starting.\textsuperscript{2} Due to the lack of a chemical reaction, electric double layer supercapacitors (EDLC’s) not only have remarkable stability with the ability to charge and discharge for up to 1 million cycles but they also have superior low temperature capability.\textsuperscript{3}

Typically the large surface-area material used in supercapacitors is activated carbon as it has good conductivity and a surface area upwards of 1000 m\textsuperscript{2}/g, equivalent to about the size of a football field with just a teaspoon of material. This material is then placed in a cell with a highly conductive, chemically stable current collector. With respect to the electrode set-up there are two main types of supercapacitor cells, symmetric and asymmetric. A typical example of both is shown in Figure 2 above.

In the symmetric set-up, both electrodes consist of a large-surface area material and both contribute a large double-layer capacitance. This effectively means that the electrodes can be thought of as two capacitors in series contributing equal capacitance. Two capacitors in series perform according to the formula:

\[
\frac{1}{C_{\text{tot}}} = \frac{1}{C_1} + \frac{1}{C_2}
\]

Where, \( C_{\text{tot}} \) is the total capacitance of the cell, \( C_1 \) is equal to the capacitance of the first capacitor and \( C_2 \) is equal to the capacitance of the second capacitor.

When both electrodes in an electric double layer capacitor device are made of the same material they have equal capacitance and when the above formula is applied we find that the device only achieves half of the capacitance of each electrode. In the asymmetric capacitor however, only one electrode contributes a large double-layer capacitance, whilst the other “non-polarizable” electrode undergoes a faradaic reaction contributing “pseudocapacitance”.

As a consequence the full capacitance of the double layer capacitor electrode can be harnessed, resulting in approximately double the capacitance than that of the symmetric device. The energy available in a supercapacitor cell can be calculated according to a simple formula:

\[
E = \frac{1}{2} CV^2
\]

Where, \( E \) = Energy, \( C \) = Capacitance and \( V \) = Voltage

In an asymmetric supercapacitor the capacitance is double that of a symmetric device and so the energy obtainable is doubled. The positive electrode of the supercapacitor is fundamentally very similar to that used in battery systems at present. This leads to the alternative name hybrid “supercapacitor” as it utilizes both battery and supercapacitor technology. Another advantage is that the use of a non-polarizable electrode results in a larger voltage window. This typically changes from less than 1.2 V in a symmetric cell with aqueous electrolyte, to 1.4 V in an asymmetric device.\(^4\) It may not seem like much but as can be seen in the formula the energy is proportional to the voltage squared. As a result the total energy available from an asymmetric device can be over three times that of a comparable symmetric system. As both have similar power capability, the real advantage of an asymmetric capacitor comes in the increased energy available. This is very important for applications that need high power and considerable energy, such as engine starting or regenerative braking.

Larger voltage windows can be achieved in supercapacitors built with an organic electrolyte resulting in an increase in energy per cell. This can also have some major disadvantages however. Typically these supercapacitors need to be very well-sealed to prevent contamination from oxygen or moisture from the atmosphere as well as to prevent gas from escaping from the cell. The electrolyte is usually highly flammable and in a sealed environment it can be explosive. For battlefield situations this would be an unnecessary vulnerability. Even in everyday applications such as regenerative braking or engine starting it could be a potential hazard. This is compounded by the fact that when an organic cell vents due to increased pressure or overcharge it results in a failure of the cell.
A cell failure is typified by a permanent breach of the hermetic seal of the cell and results in the escape of solvents such as acetonitrile which decomposes into hydrogen cyanide. In contrast, an aqueous cell will release a minor amount of oxygen, along with small amounts of hydrogen through a vent which then reseals to keep the integrity of the cell intact. Due to the nature of a cell failure which contains an organic electrolyte, it is very important to make sure that individual cells do not over-potential when in a module. This requires the use of electronics for cell balancing and monitoring in order to ensure the safety of the system. The ability of aqueous supercapacitors to vent and re-seal negates the need for cell balancing.

**Applications for asymmetric nickel capacitors**

In a typical engine, a lead-acid battery is used both to start the engine and to run the electronics while the vehicle is in operation. These two functions require somewhat different power capabilities. To start an engine requires a large amount of current, and therefore power, and a non-trivial amount of energy. However, once the engine is running the current draw is quite low, but the energy still needs to be substantial enough to keep the vehicle in operation. A supercapacitor can replace the battery for the first of these functions, engine starting. It can easily provide the power to start, over a much wider temperature range and due to the far superior cycle life, a supercapacitor will usually last as long as the life of the vehicle; it will also have enough energy for multiple attempts. As shown in figure 3, cranking an engine at -40°C from supercapacitors installed in parallel with lead-acid batteries results in peaks of current for the supercapacitors (1625 A) which are three times higher than for the lead-acid batteries (490 A). Since the lead-acid batteries are less solicited, not only do fewer need to be installed but their lifetime is also increased. And in situations where a battery completely fails to perform, a supercapacitor will be capable of starting the engine by itself. This aspect is important as a battery failure can occur during critical moments such as in a battlefield under extreme temperature conditions or even in a regular environment with a battery whose energy is drained carrying out other functions.
Figure 3  A coldstart engine starting test at -40°C; the majority of the current is drawn from the Saft Nickel Capacitor.

Supercapacitors are currently utilized in a variety of engine starting applications and have the capability to be sized for almost any type of engine. They can operate down to temperatures as low as -50 °C and up to +50 °C. They can also discharge over a wide range of currents with capabilities of more than 1000 A for short periods of time with peak 3 s cold cranking amp (CCA) current up to 2000 A or more. They may also provide smaller currents (<100 A) for more extended periods (> 1 minute). The charging time for a supercapacitor is typically quite short (< 2 minutes) and they can be charged from a battery that itself has a very small amount of charge remaining.
The principle behind this is that a supercapacitor does not require a large amount of energy to be fully charged and a battery with a low amount of charge will still have a high potential. If a battery could store 100 times the amount of energy as a supercapacitor and yet only had 1% of charge remaining, it could still almost fully charge the capacitor, providing the maximum operating voltages were similar. Currently most supercapacitors are used in large diesel truck engines. They reduce the number and size of batteries required in the truck by 50% and double the battery lifetime. The most important parameters to know when selecting a supercapacitor for engine starting, as well as most other applications are, engine size, operating temperature and rated voltage range. The size of the engine will determine how much current will be drawn, and therefore the power requirements of the supercapacitor. It will also indicate the amount of energy needed for a successful start including after multiple attempts. A decrease in temperature has a negative effect on both the power and energy of a supercapacitor and so if the vehicle is operating in a low temperature environment perhaps a larger sized supercapacitor would be needed than at room temperature. Supercapacitors can still function quite well all the way down to -50°C. An example of a 32 V, 120 KJ, Saft Nickel capacitor discharge curve at -50°C is shown in figure 4. Often a DC-DC converter can be utilized in a cold-temperature environment to increase the operating voltage and extract as much of the available energy as possible from a supercapacitor. In the discharge curve we can still see impressive energy storage even under exceedingly cold temperatures. Asymmetric capacitors utilize both a large surface area material as well as a battery-type electrode (NiOOH) originally developed for Nickel-Cadmium (Ni-Cad) batteries. As discussed above, when combined in this hybrid asymmetric device it has similar power capability to a traditional supercapacitor and even larger energy storage ability.
The applications for supercapacitors are currently not just limited to large truck engines; any type of gas or diesel vehicle with an electric starting system can be equipped with a supercapacitor, e.g. locomotives or cars etc. Asymmetric nickel capacitors are one of the best candidates for these applications due to their superior energy storage. Their capabilities do not lie solely with engine starting however. The fast charging and discharging capabilities of supercapacitors represent enhanced ability to capture the energy produced during regenerative braking, as well as quickly discharging that energy for greater acceleration. It could be used in conjunction with a battery system on electric or hybrid vehicles for enhanced efficiency, or as a standalone system in a regular internal combustion engine vehicle to eke out extra miles per gallon, similar to a flywheel. With the ever expanding green energy market and the increasing price of oil, these capabilities offer an economical alternative to a standard gas-vehicle.

Alternatively, non-vehicular opportunities include emergency power systems whereby a capacitor will react to a loss of electricity in a critical environment by immediately providing power to keep the facility operating whilst back-up power generators come on-line. Usually there can be a delay in getting the power back to a high level while the reserve power units...
come on-line. Supercapacitors can perform this function with ease and bridge the gap between the power shut-off and battery or generator back-up. Other applications could include windfarms, ski-lifts, elevators, moving platforms, cranes and just about any electrical system that requires a lot of power to do heavy lifting, moving or short-term energy storage. Supercapacitors can be incorporated quite easily into the electrical systems and do not require any further maintenance or replacement.

**Conclusion**

In conclusion, supercapacitors represent an economical and safe product that can be incorporated into a plethora of different applications with ease. They can provide superior performance for much of the applications currently available at a lower long-term cost. With engine starting they can actually double the life of the battery and reduce the number of batteries required by 50 %. Along with these benefits, the guaranteed starting capability in extreme environments even after a battery has been fully drained would be a valuable asset. Asymmetric nickel supercapacitors in particular offer an even better energy storage capability than a standard symmetric design giving an even higher likelihood of success at even lower temperatures, and reducing the size requirement. They also represent a safer and more dependable alternative to supercapacitors based on organic electrolyte with no toxic, volatile materials and a non-flammable electrolyte.

**References**

2. A. Beliakov, “Russian Supercapacitors to Start Engines”, *Battery International*, 102 (April, 1993)


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