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Scotty, We Need More Energy! - Part 2 -

DOUBLE-LAYER CAPACITORS

Technical paper by Alexander Schedlock



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Double-Layer Capacitors

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Introduction

Sustainability, clean energy, and energy efficiency are objectives that have become more important as environmental conscience steadily grows in our society. This conscience influences many new designs in electronics, which often suffer from the lack of suitable energy storage devices. A good energy storage device is increasingly key to many ongoing developments, especially for the storage of excess energy, which is produced during power generation and recuperation. These storage devices help vehicles to become cleaner, and enable wind turbines to harvest the wind more efficiently while defying the weather. From small handheld applications in everyday life to large scale power plant technologies: energy storage devices are needed everywhere in power electronics. How can energy storage devices meet these versatile challenges and how is their sustainability?

Is the Double-Layer the Solution?

The double-layer capacitor has the reputation of being a low-tech component. Only recently, this technology moved back into focus, because it has properties that are advantageous compared to other energy storage technologies. The technology of the double-layer capacitor is based on the charge storage in the so-called "double-layer". The theoretical foundation was already laid in 1853 by Hermann von Helmholtz, but it took more than a century before the first double-layer capacitors could be mass-produced. Today, they are known under different names: supercapacitors or ultracapacitors, but their physical working principle is identical.

The construction of an EDLC (Electric Double-Layer Capacitor) is simple and it was described in detail in the previous article "Scotty, We Need More Energy (Part 1)" by the author. Two electrodes form the basis of the construction. The electrode material (usually activated carbon, graphene structures or carbon nanomaterials) is applied to an electrically conducting collector and forms both electrodes of the capacitors. A membrane, the so-called separator, separates them from each other and protects them from short-circuits. The separator is permeable to the ions of the (usually liquid) electrolyte. The electrolyte functions as an ion supplier, which are the carriers for the electric current through the EDLC (Fig. 1).

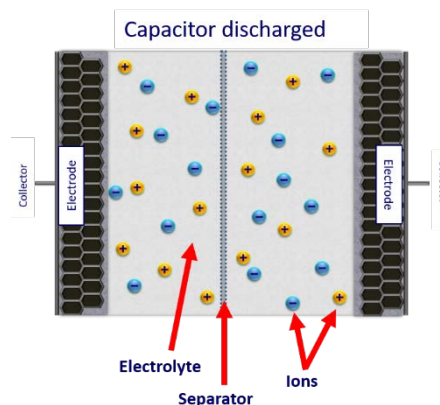


Figure 1: Schematic representation of an uncharged

When a voltage is applied, the positively and negatively charged ions migrate in opposite directions to the electrodes. There they collect at the phase boundaries between the solid electrode and the liquid electrolyte and form the so-called double-layer. At the double-layer, ions from the electrolyte face the counter ions from the electrode. The solvent molecules that separate the charges from each other are polarized by the electric field. Each double-layer is similar to one plate capacitor. In total, each EDLC consists of two "plate capacitors" connected in series (Fig. 2).

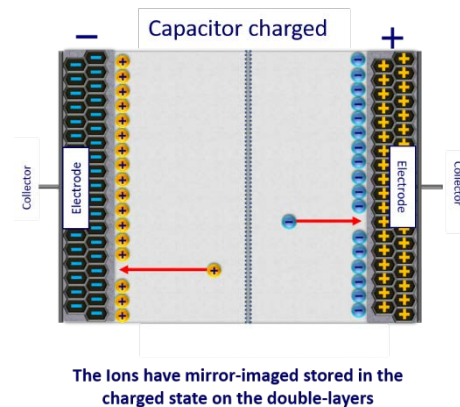


Figure 2: Schematic representation of a charged

Because the dielectric is formed by merely a single layer of solvent molecules, the distance between the "plates" of the capacitor is very small. Together with the large surface area of the electrodes, the EDLC has a capacitance according to the equation (1).

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \quad (1)$$

The Electrodes Make the Difference

A prerequisite for forming a double-layer is a suitable electrode material. About sixty years ago, the first investigations into newer storage methods and materials were conducted. Right from the beginning, activated carbon served as electrode material. Eventually, researchers looked at other materials for their suitability for use in double-layer capacitors and further developed these. The most commonly used electrode material today is activated carbon. Even though activated carbon is only a moderately conducting material, it has a high porosity, which yields a large surface area relative to its volume (Fig. 3).

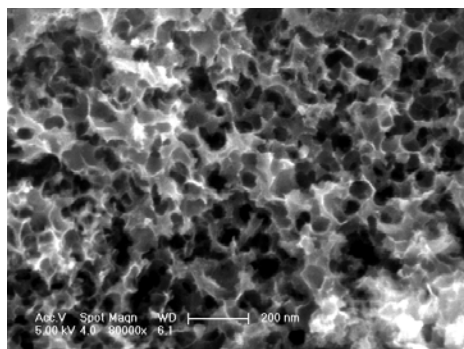


Figure 1: Activated carbon pore structure

Figure 3 shows the sponge-like structure of the activated carbon in 80,000 times magnification. With a density of up to 0.5 g/cm^3 and a (theoretical) surface area ranging from $1000 \text{ m}^2/\text{g}$ to $2000 \text{ m}^2/\text{g}$, a large surface in a small volume can be obtained. Together with its low production cost, activated carbon is the premier choice material for double-layer capacitors. The greatest strength of the material is also its greatest weakness: the pores of the activated carbon are present in different dimensions and limit, depending on their size, the available area for forming a double layer. The ions involved in the formation of the bilayer are "solvated", i.e. surrounded by solvent molecules from the electrolyte. With this shell, they can move only slowly into smaller pores, the result being an increased ESR. At the same time, the so-called micropores reduce the surface available for the double-layer, which in turn leads to a reduced capacitance (Figure 4).

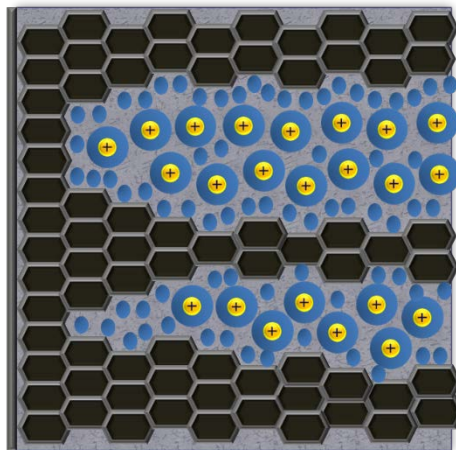


Figure 2: Different pore dimensions

The carbon structures are electrically conductive only along the crystal structures of the honeycomb carbon atoms, while the conductivity in between the lattice structures is relatively poor. The disordered macroscopic structure of the activated carbon also limits its conductivity, which is reflected in a likewise increased ESR.

A possible way to improve on ESR is the utilization of highly conductive polymers. These can be inserted in the activated carbon structure as so-called binders and they significantly increase the conductivity by electron conduction. This is also the focus of current research: improved polymers as binders should not only enhance the mechanical stability, but also increase conductivity. A suitable process control in the production of the activated carbon electrodes allows to generate specific pore sizes. This leads to an optimal utilization of the surface in the activated carbon.

Another factor that needs to be controlled by the manufacturer is the layer thickness of the activated carbon: While an excessively thick activated carbon layer leads to a decrease in the power density, too thin layers lead to a decrease in the energy density.

Many manufacturers of EDLCs are trying to increase the conductivity by using single- or multi-walled carbon nanotubes. This approach appears to be not so promising in the view of ever-increasing requirements for larger energy densities.

Long Lifetime and Cycle Stability

Double-layer capacitors are frequently associated with a high number of possible charge- and discharge-cycles and a long operational life time. In the formation of the double-layer, no chemical reactions are involved, unlike in a lithium-ion battery. In EDLCs, only the adsorption of ions takes place. But even though this process should be repeatable indefinitely, some limiting factors must be considered when operating double-layer capacitors.

Voltage is an important stressor to EDLCs: higher voltage causes a higher charge and thus more capacitance, but it also causes high electric field strengths within the component. Beyond a certain threshold voltage, the electrolyte partially decomposes when charging. The decomposed substances accumulate in the pores of the electrodes and clog them. The effective surface is reduced, which reduces the capacitance. The decomposition process results in a limited lifetime defined by the number of possible charge and discharge cycles. Electrolytes with a higher decomposition voltage can increase the number of cycles, but result in lower capacitance and higher ESR values.

Of crucial importance is also the ambient temperature during operation, because higher temperatures not only accelerate the decomposition processes but also the loss of electrolyte due to dehydration. Which limits the life of the capacitor as a time-limiting factor.

The electrolyte impacts cycle life, capacitance, the ESR, and the operational life of the capacitor. The electrolyte must be chemically inert, so it doesn't react with the electrode material. It should have a high decomposition voltage and be a good ion source for the double-layer. The choice of the appropriate electrolyte is therefore just as important as the selection of the electrode material. Proper use and compliance with factory limits set by the manufacturer are essential to ensure a long life for the capacitors.

Supercapacitors – More than just a Predecessor of the Lithium-Ion Capacitor

The double-layer capacitor has a long history of research and development, while commercial mass production lasts only a few decades. It was just in the past decade when the high potential of the technology has been recognized and the further development of supercapacitors was set into motion.

At a short first glance, lithium-ion capacitors could replace double-layer capacitors. However, the developments of both technologies follow different targets: while the development of the lithium-ion capacitor focuses on high energy density, the EDLC aims at high power density. This also differentiates the target applications of the two technologies, so that they are not in direct competition, but rather complement each other.

EDLC technology boasts with its particularly large power density. The high proportion of double-layer capacitance allows to charge and discharge the capacitor very quickly. In this discipline the EDLC is superior to the electron transfer of the lithium-ion capacitor. As a consequence, an EDLC can pick up and release higher currents in the same time frame compared to a LiC. The table shows the specific parameters of the EDLC compared to the lithium-ion capacitor (LiC) and the lithium-ion battery (LiB).

	EDLC	LiC	LiB
Anode	Activated Carbon	Activated Carbon	LiCoO ₂ / LiMnO ₄
Cathode	Activated Carbon	Graphite/Li-Ion doped	Graphite
Electrolyte	Organic Solvent	Organic Solvent	Organic Solvent
Temperature Range	-40 ~ +85 °C	-25 ~ +70 °C	-25 ~ +45 °C
Max. Operating Voltage	2.3 ~ 2.7 V	3.8 ~ 4.0 V	3.7 ~ 4.2 V
Max. Charging Rate	~ 1,000 C	~ 100 C	0.5 ~ 1 C (normal)
Volume/Mass	small	small	large
Charge-/Discharge-Cycles	> 500,000	500,000	1,000
Self-Discharge Rate	> 70 % (2000 h)	< 5 % (2500 h)	< 5 % (2500 h)
Safety	Intrinsically Safe	Intrinsically Safe	„low risk“ depending on materials and construction
Energy Density	(5 ~ 7 Wh/kg)	(30 ~ 50 Wh/kg)	(~250 Wh/kg)

The charging rate of EDLCs is superior compared to other technologies. With this feature, an EDLC is suitable for coping with large charging currents, for example in braking circuits. It is therefore often used to realize the energy recuperation in electric vehicles. This also protects the life of the batteries and at the same time leads to energy savings. In wind turbines, EDLCs power the emergency tilt control system, which safely shuts down the system in case of power failure or excessive wind speed. This protects the turbine from mechanical damage. Previously, lead-acid batteries were used here for many years, which have a shorter life than EDLC and thus increased the maintenance effort. Due to their longevity and high cycle stability, double-layer capacitors help to minimize maintenance and thus reduce operating costs.

Although the double-layer capacitor has already been used in many applications, it is not always the optimal choice. An example of this is a mobile EDLC application, the “On-Board Units” of the Toll Collect System. Here, an EDLC provides the energy for the short, but intense data transmission. A disadvantage of this application is the large leakage current of double-layer capacitors, that often even exceeds the charging current. However, lithium-ion capacitors have a significantly lower leakage current. In combination with batteries or a photovoltaic panel, the LiC can be charged without losing the charge. The same issue is found in energy harvesting application, where lithium-ion capacitors offer also the superior technology vs. EDLC.

Summary

For a long time, double-layer capacitors had merely a niche existence and were considered being low-tech devices. Over the past decade, numerous improvements in materials and process management have made the technology evolve and become more widely used in a variety of applications. Now, the double-layer capacitor has become a high-tech product. Precise process control, which enables a structured layering of carbon atoms, as well as chemically sophisticated electrolytes have matured into a technologically demanding mass-produced product. Technologically, however, the double-layer capacitor reaches the physical limits. As a result, further developments such as the lithium-ion capacitor are becoming increasingly important. Because as a new branch of the supercapacitor family, which could develop into the largest competitor of traditional battery systems, hybrid capacitors have a greater potential to succeed than double layer capacitors.

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Company

Jianghai Europe Electronic Components GmbH, with headquarters and warehouse in Krefeld, Germany, supports the European customers of Nantong Jianghai Capacitor Co., Ltd. (Jianghai) in Nantong, China. Jianghai was founded in 1958. While Jianghai developed and produced in the beginning specialty chemical products (such as electrolyte systems), from 1970 it started the design and production of aluminum electrolytic capacitors. Pre-material production, e.g. for etched and formed anode foils, was vertically integrated. Film-, polymer and Energy-capacitors complement the product portfolio. Jianghai is the largest Chinese manufacturer of e-caps and one of the three leading manufacturers of snap-in and screw terminal type capacitors in the world.

Author



Alexander Schedlock graduated from the College of Engineering “Heinrich-Hertz-Berufskollege” in Dusseldorf as a state examined technician specializing in electrical engineering. After successfully completing his apprenticeship as an IT system electronics engineer (2010), he worked as a field service technician and was thus able to gain experience with computer terminals for various applications. In addition, he studied for four years at the technical school for electrical engineering and graduated in 2017 successfully from his state vocational school exam. Since 2018 he works in the sales team of Jianghai Europe Electronic Components GmbH as Technical Sales Manager and supports customers in technical designs throughout Europe. Mr. Schedlock is in charge of the Energy-Capacitors.

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