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Scotty, We Need More Energy! - Part 1 -

LITHIUM-ION CAPACITORS

Technical paper by Alexander Schedlock

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Lithium-Ion Capacitors

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Introduction

Due to their high energy density and low self-discharge, batteries are widely considered as possible energy storage devices of the future. However, batteries also have disadvantages such as low power density and limited cycle life. Misapplication of batteries may even cause a fire hazard. Their construction requires the use of certain rare metal oxides, which sometimes originate from controversial sources.

Many applications require energy storage devices that enable the mobile use of devices in the first place. Another solution is a component that has always been an integral part of electronics: the capacitor. A component that stores energy, but was previously inferior to the battery. Although developments such as super-capacitors and double-layer capacitors (EDLC) achieve much higher power densities than batteries, they could be used as the sole power supply only in rare cases. However, supercapacitors, with their excellent cycle stability, are far superior to battery systems and safer in operation.

A young technology combines the advantages of supercapacitors and batteries. It is named "Lithium Ion Capacitor" ("LiC") and closes the gap between the traditional capacitors and batteries. The company Jianghai offers this technology under the concept of “Energy Capacitors” or “Energy-C” in Europe. The author works there as a specialist in Energy-Cs.

Lithium-Ion Capacitor - the Energy Storage of the Future

The storage capacitance for electric charges in both the lithium-ion capacitor and in the double-layer capacitor is based on the existence of two types of capacitance: the electrostatic double-layer capacitance and the electrochemical pseudo-capacitance. Both together yield the total capacitance of the respective capacitor technology. Although the capacitances are coupled, one can distinguish between their related charges. The specific properties of the components can be optimized. A small excursion into physics shall clarify the nature of the two capacitances.

Double-Layer Capacitance "Helmholtz Double-Layer"

Over the past century, several models have been developed that describe the double-layer capacitance. Hermann von Helmholtz, however, was the first to study the principle of the double layer and present it in a model of the so-called "Helmholtz double layer". His model was the first to describe how electrical energy is stored in double-layers.

In today's EDLCs (Electric Double-Layer Capacitors), this charge storage is optimally utilized. The constructive basis of the capacitors consists of two activated carbon electrodes, which are applied to an aluminum foil, the collector. The electrodes are separated from each other against short circuit by a membrane (the so-called separator), which is permeable to ions. At the same time the membrane serves as a reservoir for the liquid electrolyte. The liquid electrolyte supplies ions as carriers of the electric current through the capacitor. When a voltage is applied, the ions in the electrolyte migrate to the opposite polarity electrode. The ions collect at the phase boundary (boundary between liquid electrolyte and solid electrode) and form a double layer (Fig. 1).

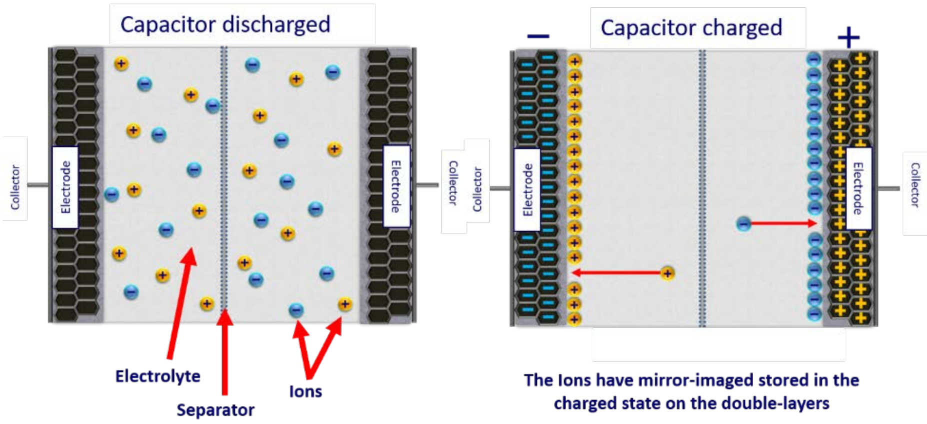


Figure 1: Schematic representation of a double-layer-capacitor (charged/ discharged)

The double-layer consists of ions from the electrolyte and a layer of counter ions in the electrode. An electric field is formed between the two charge carriers, which polarizes the molecular layer between them and isolates them from each other. It has a "charge-separating effect" and separates the two layers like the dielectric of a plate capacitor. This layer is also called "inner Helmholtz Layer". Together with the ion layer in the electrolyte ("outer Helmholtz layer"), these layers are called double-layer (Fig.2). In simple terms, two plates are formed, which are separated by a dielectric. The formation of the double layer happens very fast because the ions are only adsorbed and do not form a chemical bond. This allows in particular for the fast formation and disappearance of the double layer (or charge and discharge of the capacitor).

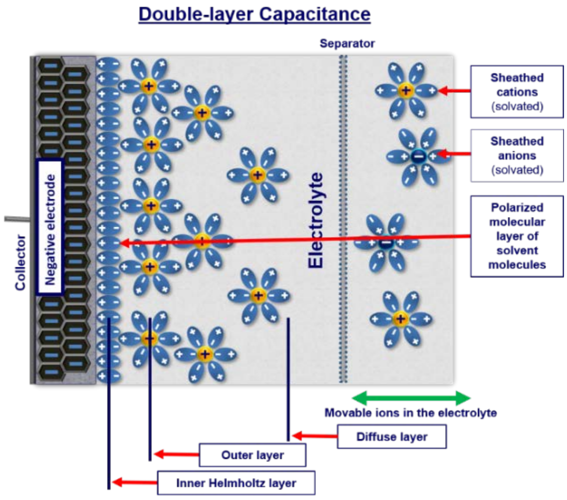


Figure 2: Schematic representation of the double-layer

The totally stored charge of the double layer is dependent on the ions in the electrolyte and the ions in the surface area of the electrode and increases linearly with the applied voltage up to a limiting value. This limit is also called the decomposition voltage of the electrolyte.

Because a double layer is formed at both electrodes when a voltage is applied, this corresponds to a series connection of two plate capacitors. Accordingly, the formulas for calculating the electric field and the capacitance apply. The capacitance of symmetrically designed electrodes corresponds to the capacitance of a single electrode.

$$\mathrm{E} = \frac{U}{d} \qquad \mathrm{C} = \varepsilon_0 \varepsilon_r \frac{A}{d}$$

The formula for calculating the capacitance shows that the capacitance is proportional to the area of the plates and reverse proportional to the distance between the plates. Activated carbon as electrode material offers the advantage of a very large surface area due to its highly porous structure. The distance between the ionic layers is very small due to the thin separation layer of molecules. The distance ranges (depending on the electrolyte used) from 0.1 nm to 10 nm. As a result, double-layer capacitors usually offer very high capacitance values. An important constraint arises from the small distance: the limitation of the permissible operating voltage. Excessive electrical field strengths may cause dielectric breakdown of the dielectric. The limiting factor here is the stability of the molecular binding of the separating solvent molecules. This stability is limited and hence the double-layer can only exist in the voltage range between 1.2 V and 3 V. Beyond this range, the separating character of the double layer gets lost, short circuits may occur and electrolysis begins, which in turn leads to irreversible damage to the electrolyte.

Electrochemical Pseudo-Capacitance

Early studies of double-layers showed different results between the measured capacitance and the theoretically calculated capacitance of the components. The measurement results were significantly higher than expected and thus unexplained. The phenomenon was first mentioned by Grahame in his modified star model, in which he proposed a "specific adsorption". But only a few years later, the foundation for the so-called pseudo-capacitance was laid.

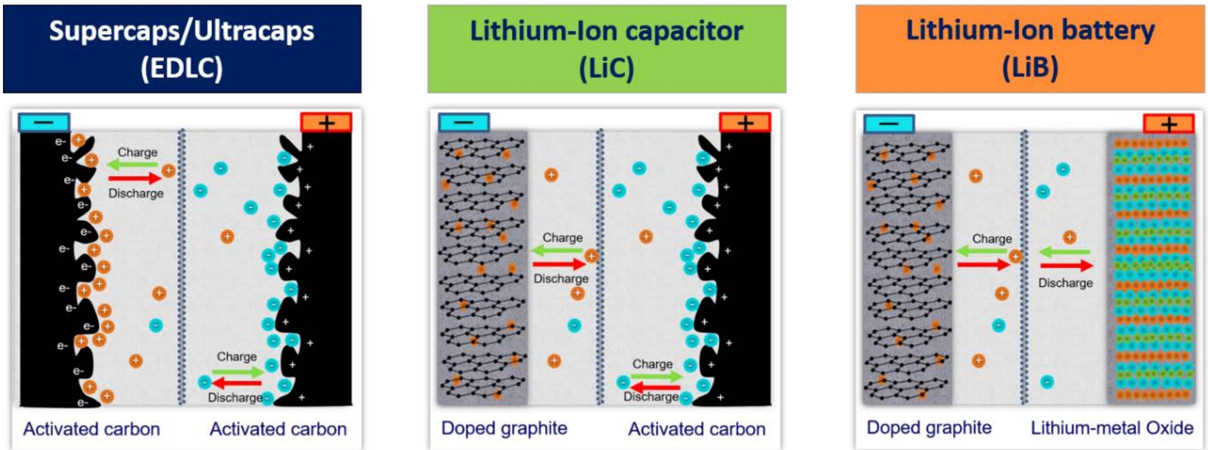
The pseudo-capacitance (or Faraday charge) is an integral part of the double-layer. It is created when ions strip their molecular shell, cross the separating layer and touch the electrode surface. They remain attached to the surface by weak van-der-Waals forces, causing a so-called Faraday charge transfer, in which the adsorbed ion passes on charges to the surface ions in the electrode. However, no chemical binding with the electrode occurs: there is merely an electron transfer. This process is reversible and it is actually being reversed when discharging, which basically could be repeated indefinitely. The multistep redox reactions in batteries follow a similar principle, but differ significantly from the charge exchange in pseudo-capacitances. Redox reactions rely on "real", i.e. chemical reactions, associated with bonds. Although the reactions are in principle reversible, in the course of many charge and discharge cycles chemical compounds form that cannot react any further. This leads to the loss of capacitance.

The electron released during the electron transfer travels to the opposite electrode via the external circuit. At the same time, many oppositely charged ions travel through the electrolyte to the electrode which absorbs the ions. When discharging, the electron is released again. This electron exchange is very fast - much faster than the chemical processes in a battery. This allows for a high power density.

The storage capacitance of the pseudo-capacitance shows a significant difference to the double layer. Both pseudo-capacitance as well as double-layer capacitance rely on the potential-dependent degree of coverage of the electrode surface by adsorbed ions. The difference, however, is that in all pseudo-capacitance reactions the ions are desolvated, i.e. they are not surrounded by a shell of solvent molecules. They are thus significantly smaller than the “sheathed” ions of the double layer. Theoretically, the pseudo-capacitance of identical electrode surface area can be 100 times larger than the double-layer capacitance. The property of forming a particularly large amount of pseudo-capacitance depends on the type of electrode material. For example, metal oxides of transition metals are used, some of which are introduced into the electrode material by doping. Conductive polymers applied to the structures of carbon electrodes are also suitable for creating pseudo-capacitors. However, there are no capacitors which rely solely on pseudo-capacitance. In real pseudo-capacitors the double-layer capacitance ranges from 5 % to 10 %.

The best of both Worlds: Lithium-Ion Capacitors

Lithium ion capacitors combine the advantages of EDLC and batteries: the large power density of EDLC combined with the high energy density of batteries. The construction of a lithium-ion capacitor is similar to that of an EDLC. One of the active carbon electrodes used is identical in construction to the double-layer capacitor. The second electrode was replaced with a high pseudo-capacitance electrode consisting of lithium ion-doped graphite.



Graphite consists of layered graphene. Graphene has a carbon structure in which each carbon atom is bonded to three other carbon atoms, forming a two-dimensional lattice of hexagonal carbon compounds. Each of these carbon atoms is connected to a carbon atom of the adjacent layer. By doping, positively charged lithium ions are inserted between the graphite layers in order to enhance the electrical conductivity and the pseudo-capacitance formation. During electron transfer, the "electron-hungry" lithium ions (and not the migrated electrolyte ions) take the electrons. The doping of lithium ions into the carbon material at the negative electrode lowers its potential and causes a voltage of at least 2.2 V at the terminals of the uncharged capacitor. To charge the capacitor, a voltage larger than the terminal voltage of the capacitor is required. During the charging process, the potential of the negative electrode is lowered by 0.5 V and the positive double-layer electrode is applied with a voltage of up to 1.3 V. This results in output voltages of up to 4 V. Since the amount of energy stored in the capacitor increases quadratically with the voltage, the charge carrier density of about 4 V lithium-ion capacitors is more than twice as high as that of double-layer capacitors with 2.7 V.

Scotty, We Need More Energy!

Many applications require more and more energy for their long-term operation. This requirement adds a new challenge to new energy storages. The lithium-ion capacitor serves as a link between capacitors and batteries and offers an advanced solution to this challenge. The lithium-ion capacitor enables the design of new applications that were formerly not possible.

The Chinese manufacturer Jianghai already mass-produces lithium-ion capacitors of various types. Whether as a radial or snap-in capacitor shape or in pouch type to go into larger modules. The modules be customized to fit a wide variety of applications and it can be optimized in many ways.

A classic example is the energy recovery when braking a load. This can be with a forklift in the warehouse, an elevator in the house, a car on the street or a train on the track. When braking, energy is generated, which today is usually dissipated as heat, either mechanically or through a resistor. Braking currents are often too large for a conventional battery system and would further reduce its already limited life. Their low cycle stability prevents batteries from being used for energy recuperation systems.

With its large power density of up to 8.5 kW/kg, a LiC can store and release the energy recuperated from braking. Safety and reliability of LiC enable usage as the main energy storage device for applications such as driverless transport vehicles or in e-mobility. In China, pilot hybrid bus fleets are already utilizing this innovative energy storage system. The buses are equipped with a module that replaces the existing battery. Replacement reduces the volume and weight of the bus. The reduced distance range is no real constraint because of the low charging time for the new module. Charging takes place at bus stops according to the "charge-and-go" principle: while passenger enter and leave the bus, the charging is conducted. This operation mode allows passengers to be continuously transported without lengthy loading pauses.

Summary

The lithium-ion capacitor as a powerful variant of the double-layer capacitor boasts with energy densities that previously could only be offered by batteries. The innovative nature of this emerging technology is to enable the powering of applications that previously had no solution.

While the first generation of the lithium-ion capacitor is already a mature mass-produced component, Jianghai is working on the next generation. The development target for the coming years are energy densities of more than 50 Wh/kg and power densities in the range of 30 kW/kg. This will qualify the Lithium-Ion Capacitor to become the energy storage of the future.

Additional Information

Jianghai offers various solutions according to the application profile with the “Energy-C” concept. Please contact the author at ccc@jianghai-europe.com in the Capacitor Competence Center for further questions.

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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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