

ENERGY SERIES

ENERGY STORAGE – BATTERIES AND SUPERCAPACITORS SET



Volume 3

**Supercapacitors Based on
Carbon or Pseudocapacitive
Materials**

**Patrice Simon
Thierry Brousse
Frédéric Favier**

ISTE

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coordinated by
Patrice Simon and Jean-Marie Tarascon

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Introduction

I.1. Why supercapacitors?

Electrochemical capacitors, or supercapacitors (SCs), are electrochemical energy storage systems that deliver or absorb large peak power [SIM 08a, CON 99].

Figure I.1 shows the advantage of using these systems and their complementarity with batteries (LFP, in this case). The figure depicts the energy density delivered or stored according to charge time. For longer charge times (low charge rates), the battery stores 20 times the energy stored in supercapacitors. When the charge time decreases (faster charge rates), the energy density of batteries decreases, whereas that of supercapacitors remains almost stable; for charge times of a few seconds, a supercapacitor can store more energy than a battery.

The two curves intersect at about 10 s, which approximately defines the usage boundary of the two systems: applications requiring a supply of energy in short bursts (power), typically less than 10 s, should be addressed by supercapacitors, whereas batteries are better suited to applications requiring a longer energy supply >10 s.

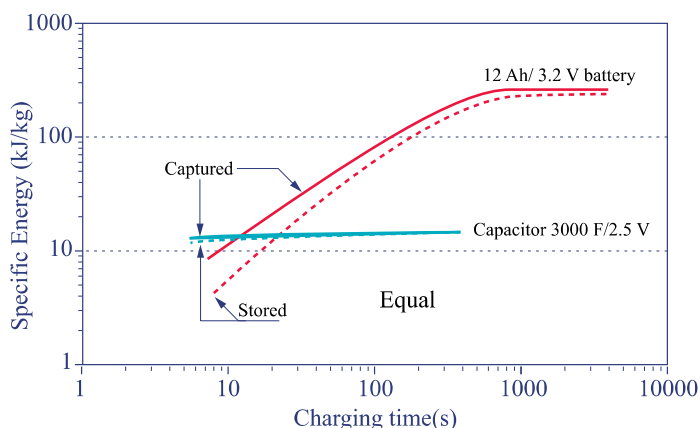


Figure I.1. Discharge curves of a 12 Ah/3.2 V LFP/graphite Li ion battery and a 3,000 F/2.5 V supercapacitor. The battery and the supercapacitor have an identical volume [MIL 08]. For a color version of the figure, see www.iste.co.uk/brousse/supercapacitors.zip

The specific features of supercapacitors are due to the charge storage mechanism which occurs at the surface of active electrode materials, unlike batteries that store the charge in the bulk of active materials through redox reactions. In supercapacitors, two main types of active materials can be distinguished, as they store charge in two different ways:

- the vast majority of supercapacitors currently uses porous carbon with a large specific surface area (SSA) as the electrode material; these supercapacitors are called electrochemical double-layer capacitors (EDLCs). They store charge by accumulating ions from the electrolyte at the surface of carbon electrodes under polarization [SIM 08a]; there are therefore no redox reactions involved;

- pseudocapacitive materials are the second family of materials used in supercapacitors. As their name suggests, the electrochemical signature of these materials seems to be capacitive, in the way that it is similar to that of a carbonaceous material (see Figure I.3); however, the storage

mechanism is different, since the energy is stored by means of fast and reversible redox reactions, usually occurring at the (sub)surface of the material. We will come back to the storage mechanisms and the properties of pseudocapacitive materials in Chapter 4 [CON 99].

I.2. Some figures

A growing number of scientific articles containing the words “supercapacitor” or “pseudocapacitor” has been published since 2003–2004. Approximately 3,000 articles contained one of these words in 2016; this highlights the current enthusiasm for these systems. When it comes to global research, France is in fifth place, primarily due to groups in Montpellier (ICG), Nantes (IMN), Orléans (CEMHTI) and Toulouse (CIRIMAT), and all members of the French Network on Electrochemical Energy Storage (RS2E). Laboratories such as IS2M in Mulhouse, LCMCP of Chimie Paris Tech or ICMCB in Bordeaux are also strongly involved in the topic as part of RS2E.

I.3. Applications

There are two main types of applications for supercapacitors depending on the format (actual capacitance) of the cells used. In small formats (capacitance lower than 50 F), supercapacitors have been used for over 20 years in the field of power electronics, for example in the development of power buffers or to supply energy to sensors. They are also found in small tools or even in some toys. The real turning point came with their use as the power supply for emergency systems in the opening of the doors of the Airbus A380, a program that began in 2005 and was developed from the design of the aircraft. Even if it is a niche market, it has, on the one hand, demonstrated the advantage of using supercapacitors for power applications, but also the maturity,

safety and reliability of this technology. Since then, the supercapacitor market has continued to develop both in small formats as well as in those with greater capacitances (several thousand Farads). Today there are many applications, most of the time in the form of modules of several tens or hundreds of volts. On tramway or trolleybus lines, they are used in network regulation, to boost charging with brake energy recovery (or the recovery of potential energy in the case of harbor cranes). Applications using supercapacitors for electric traction also exist in electric buses in the city of Shanghai [CHI 13] or even the recent electric tramway lines (2014) of the Bolloré group (*Blue Solutions company*) [OBJ 17] and the electric boat from the same Blue Solutions company [LEJ 13]. In these applications, supercapacitors are used for their capacity to recharge rapidly (within a few tens of seconds). Their autonomy is however limited by the space available to embark the SCs.

Due to significant interest in these systems, supercapacitors have also emerged in the automobile transport market. In this application, it is Citroën who was the driving force, since 2011, with the C3 and C4 including a 1.2 kW starter-alternator supplied by Continental using Maxwell supercapacitors. The starter-alternator helps to perform *stop / start* functions and regenerative braking.

Other manufacturers closely watched this technology and in 2012 Mazda embarked upon the *stop and start* venture in partnership with Nippon Chemicon.

A great deal of detailed information on the applications of supercapacitors is available at www.supercondensateur.com. This site is hosted by an enlightened amateur, passionate for new technologies and it is quite comprehensive, even if some information must be read with hindsight.

In summary, supercapacitor technology has now matured and many manufacturers explore the world of supercapacitor

cells or modules. Table I.1 lists the five main manufacturers of supercapacitors in the world. The word leader in terms of production volume and range of products is Maxwell, NessCap and Nippon Chemi-con closely follow. Nippon Chemi-con devices suffer from the use of propylene carbonate (PC) as the solvent of the electrolyte, thus reducing the power density by a factor of 2–3.

CapXX specializes in high power cells (70 kW/kg) but with lower capacities (several hundred mF), primarily in flexible prismatic formats. Blue Solutions specializes in large capacitance cells and only targets applications requiring large voltages and/or capacitances (tramways, boats, buses, etc.).

Company	Country	Product	Design	Unit voltage (V) / solvent	Capacitance (F)	Module
MAXWELL	USA	Bootscap	Prismatic and cylindrical	2.7 / AN, PC	5 - 3000	>125V
NESSCAP	Korea	Nesscap	Prismatic and cylindrical	2.7 / AN, PC	3 - 5000	Up to 340V
Nippon Chemi-con	Japan	DLCap	Prismatic and cylindrical	2.7 / PC	300-3000	>200V
BATSCAP	France	Blue solutions	Cylindrical	2.7 / AN, PC	600 - 9000	>300V
CAP-XX	Australia	CAP-XX	Prismatic (2D)	2.5 AN	0.075 - 2	N/A

Table I.1. Main supercapacitor manufacturers. Maxwell recently announced the development of a supercapacitor with a nominal voltage of 3 V

I.4. The key parameters of supercapacitors

I.4.1. Cell voltage V

The maximum potential difference at the supercapacitor terminals (V_{\max}) depends on the nature of the electrolyte and the current collectors chosen. Aqueous electrolytes have a (thermodynamic) theoretical stability domain of 1.2 V. They give rise to systems whose nominal voltage does not exceed 1.2 V as a general rule due to the redox reactions of the