

Supercapacitors

Electrochemical capacitors, also called supercapacitors or ultracapacitors, are energy devices with a high power and energy density. They can be the alternative but also support for batteries. This new generation of energy stored devices take indirect place between electrochemical batteries and dielectric capacitors. Supercapacitors can store 20-200 times more energy than conventional capacitors and release it with high power, achieve at the same time current density typical for capacitors and unavailable for batteries.

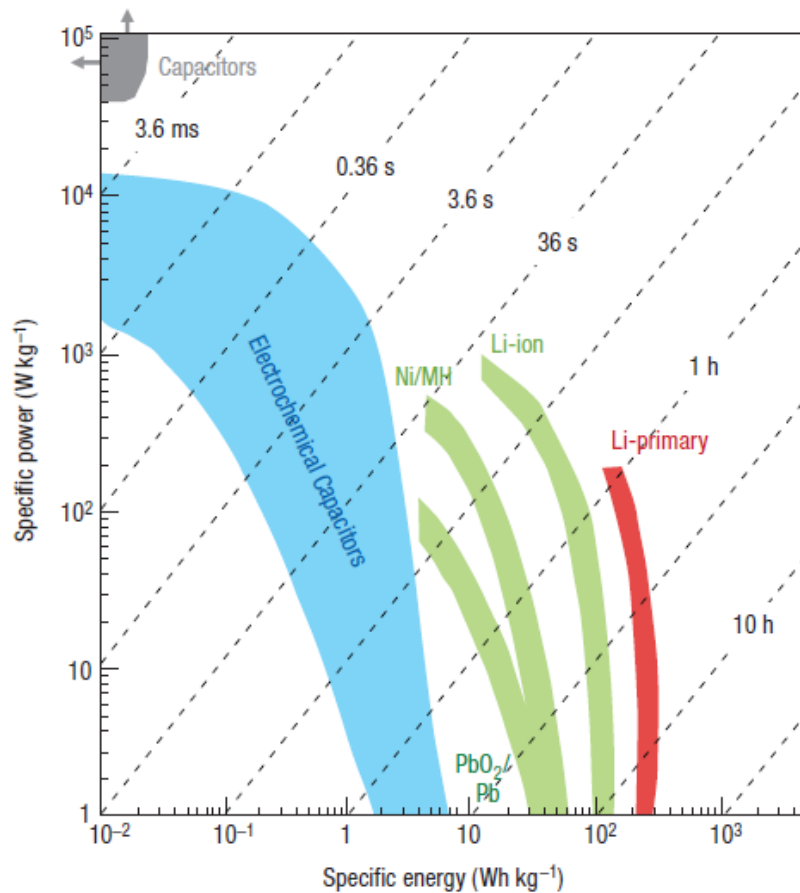


Figure 1. Ragone plot

The advantages of EC:

- They can be fully charged and discharged in seconds; as consequence their energy density is lower than in batteries,
- High power delivery or uptake can be achieved for shorter time
- Cycle efficiency, even 95%
- No material degradation
- Non toxic materials
- Safety

Application of electrochemical capacitors:

EC are used when high power demands are needed, i.e. car starting, acceleration or hills overcoming, but also in elements co-working with solar or fuel cells, and in many devices used every day, like: memory back-up in toys, cameras, video recorders, mobile phones and so forth. The main market for next few years is transportation market, including hybrid electric vehicles, as well as subways and tramways.

Supercapacitors:

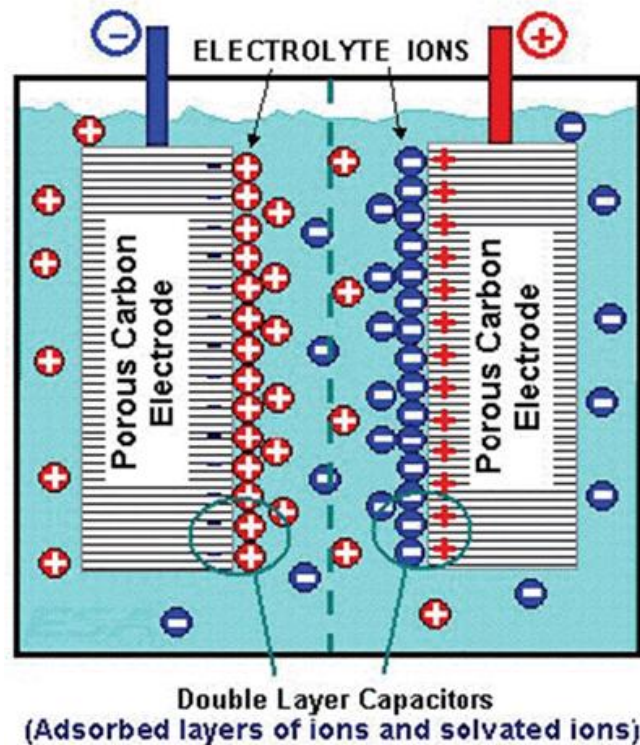


Figure 2. Scheme of Electrochemical Capacitor.

Fig. 2 shows the scheme of ECs construction. The cell is built from two electrodes made from the active material, separated with membrane (allow free ions exchange and protect against short-circuit) and solid or liquid electrolyte. Several types of ECs can be distinguished, depend on the charge storage mechanism as well as the active material type. They store energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors). EDLCs ,the most common, use carbon-based active materials with high surface area. Pseudo-capacitors or redox supercapacitors use transition metal oxides as well as electrically conducting polymers as pseudo-capacitive active materials. A third group of ECs are hybrid capacitors. They are combining a capacitive or pseudo-capacitive electrode with a battery electrode. They benefit from both the capacitors and the battery properties.

Electrochemical Double Layer Capacitors:

EDLC are electrochemical capacitors that store charge electrostatically using reversible adsorption of the electrolyte ions onto active materials that are electrochemically stable and have high accessible SSA. Charge separation occurs on polarization at the electrode-electrolyte interface, producing what Helmholtz described as double layer capacitance C :

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad \text{or} \quad C/A = \frac{\epsilon_r \epsilon_0}{d}$$

where ϵ_r is the electrolyte constant, ϵ_0 is the dielectric constant of the vacuum, d is the effective thickness of the double layer (charge separation distance) and A is the electrode surface area.

The phenomenon of electric double layer formation takes place almost on each material, which have the ability to charge conduction. EDL is created after insertion electrode in an appropriate electrolyte material and applying the external potential. The classical electrode has limited specific surface area(SSA), the interface electrode-electrolyte is limited, and this determines the efficiency of double layer formation. The good conducting and porous carbon materials provoke that electrical charge is accumulated at electrode-electrolyte interface, using the whole area of electrode pores and electrolyte. The structure of EDL shows Fig. 3.

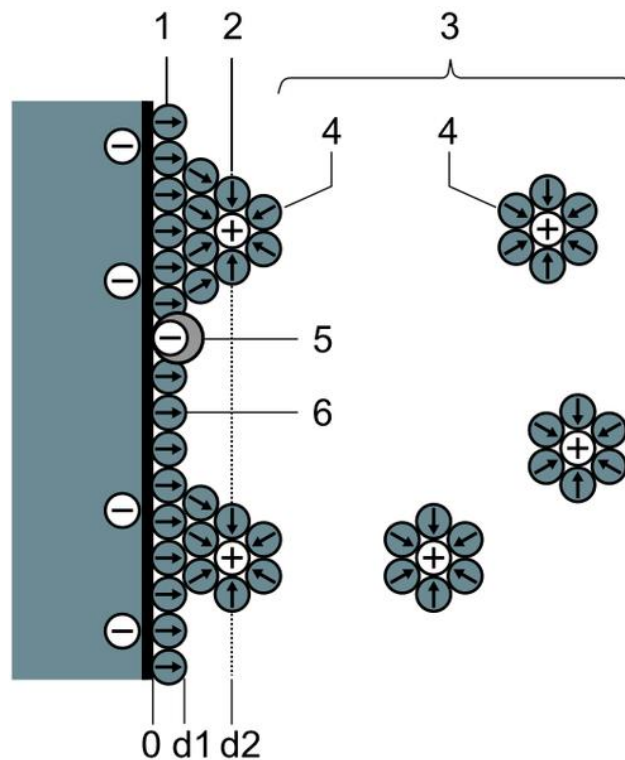


Figure3. Scheme on double layer on electrode: 1. IHP Inner Helmholtz Layer, 2. OHP Outer Helmholtz Layer, 3. Diffuse layer, 4. Solvated ions, 5. Peculiar adsorptive ions, 6. Solvent molecule.

During the charging process the migration and separation of ions is observed. On the electrode surface with the correct sign, the solvated ions form the thin layer. The EDL

structure is built from two parts: first one is created between electrode surface and inert Helmholtz layer (IHL)-it contains the solvent particles and specific adsorbed ions; the second-diffuse layer starts from outer Helmholtz layer(OHL).

The value of electrical capacitance of carbon materials strongly depends on its microstructure. Fig. 4 shows the structure and arrangement of pores in carbon.

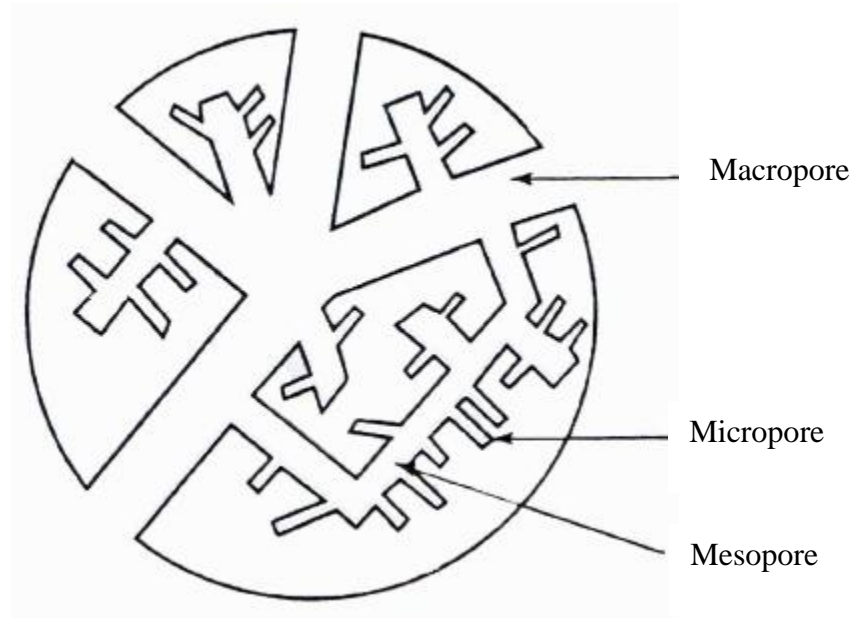


Figure 4. Structure and arrangement of pores in carbon material.

It is important to notice that in EDL creation and in adsorption processes take part pores with diameter close to diameter of adsorbed ions, mainly micropores ($d < 2\text{nm}$). Bigger pores (meso- and macropores with diameter equal respectively $2 < d < 5\text{nm}$ and $d > 5\text{nm}$) take part in ions transport.

Determination of EC capacitance:

1. Assembling the capacitor cell:
 - a) Au current collector, thickness $\sim 60\mu\text{m}$
 - b) carbon electrode-measure mass, thickness and diameter of each electrode
 - c) separator: glass fiber, thickness??
 - d) 3 different, already prepared, electrolyte: 1M H_2SO_4 , 6M KOH, Ionic liquid
2. Electrochemical testing:
 - a) Impedance spectroscopy from 100 kHz to 1mHz
 - b) Cyclic voltammetry at the scan rate 10 or 20 mVs^{-1} .
 - c) Galvanostatic Charge and Discharge characteristic in the correct voltage range.
3. Capacitance calculation

Carbon electrodes

The composite carbon electrodes were prepared by mixing 95% (w/w) of AC (CECA Acticarbon AB, from CECA company) with 5%(w/w) polytetrafluoroethylene binder (PTFE). The physical characteristic of AC material is given in the table below.

Table 1 Physical properties of CECA "Acticarbon AB" Activated carbon

BET surface ($\text{m}^2 \text{g}^{-1}$)	1428
Microporous volume ($\text{cm}^3 \text{g}^{-1}$), $<2 \text{ nm}$	0.596
Mesoporous volume ($\text{cm}^3 \text{g}^{-1}$), $2-50 \text{ nm}$	0.03
Macroporous volume ($\text{cm}^3 \text{g}^{-1}$), $>50 \text{ nm}$	0.141
Resistivity ($\Omega \text{ cm}$)	0.82
Fe content (ppm)	100

Electrochemical Impedance Spectroscopy

The capacitive behavior can be easily observed by using EIS measurements presented in the form of Nyquist plot.

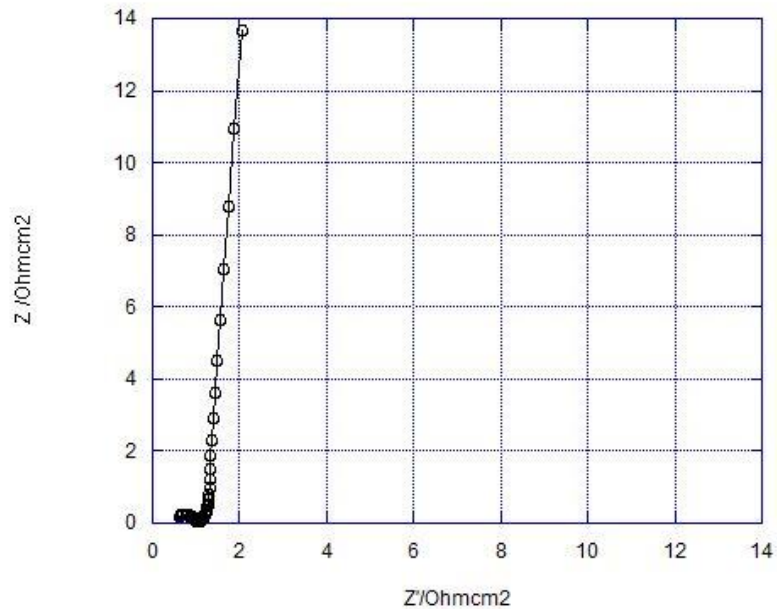


Figure 5 The impedance plot for an electrochemical system.

To determine capacity based on impedance measurement use equation:

$$C = 1/2\pi f Z''$$

where C is the specific capacitance (Fcm^{-2}), f is equal 1mHz and Z'' is the imaginary component.

Cyclic Voltammetry

For the ideal capacitor based only on electrostatic effect on the electrode-electrolyte phases, the capacitance current should not be dependent on applied external potential. Thus the typical CV curve for EC has rectangular shape. In practice changes in ideal shape depends on many factors, i.e. resistance and redox reaction influence.

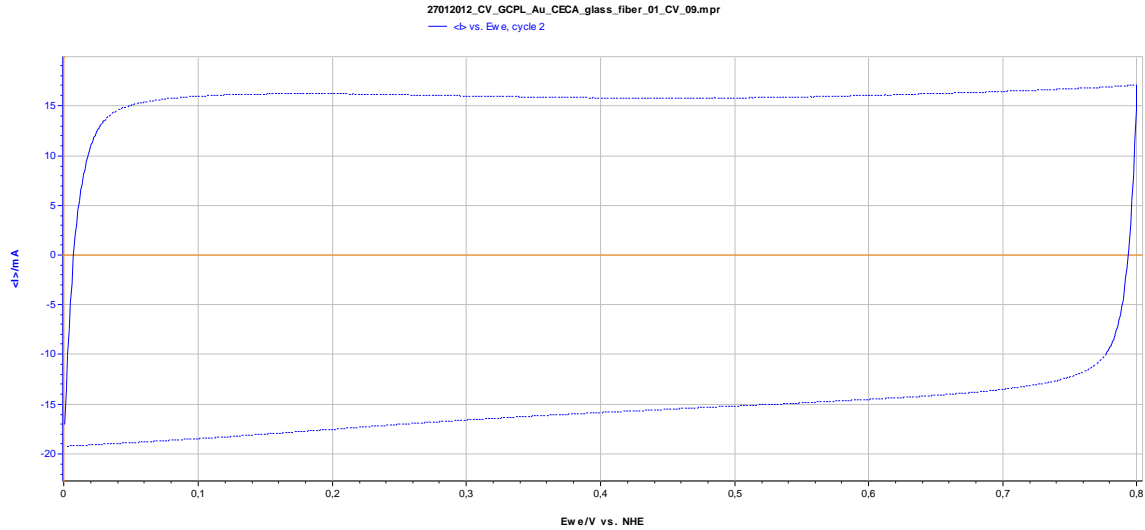


Figure 6 Typical CV curve.

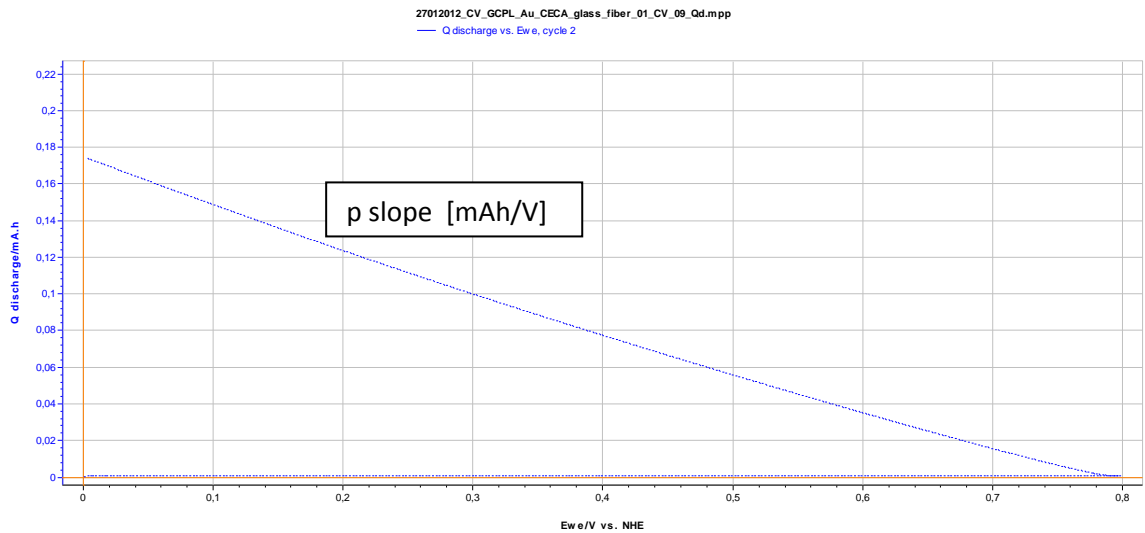


Figure 7 Qdischarge vs. Ewe plot, which is used to calculate p slope from equation below.

To determine cell capacitance from CV curve use the equation:

$$C_{am} = 2 \times p \times 3600 / m_{am}$$

where C_{am} is cell capacity given in Fg^{-1} , p is slope calculated from the Q discharge vs. Ewe plot and given in mAhV^{-1} and m_{am} is mass of active material.

Galvanostatic Charge and Discharge characteristic

This evaluation is critical to the analysis and prediction of the active materials performance under practical operating conditions. The working electrode is submitted to a constant current I (charge or discharge), and voltage versus time is recorded between minimal and maximal values.

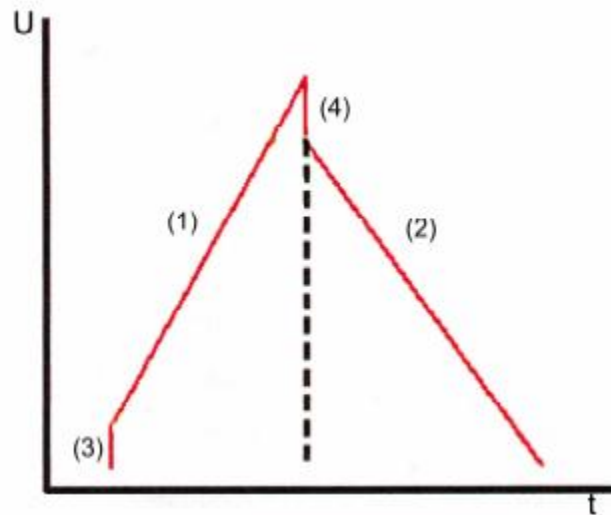


Figure 7 The typical curve of galvanostatic charge-discharge process. 1. The cell behavior during charging; 2. The cell behavior during discharging; 3. The initial process; 4. This section is responsible for the negative resistive ohmic lost associated with the resistance of the cell.

To determine the gravimetric capacitance use the equation:

$$C_{am} = 2 \times I / p \times m_{am}$$

Where I is the applied current (A), p is the discharge slope calculated from GCPL plot and m_{am} is the active material mass.

References:

1. Conway BE. Electrochemical supercapacitors: scientific, fundamentals and technological applications. New York: Plenum; 1999.
2. Beguin F., Frackowiak E. Carbons for electrochemical energy storage and conversion systems. CRC Press; 2010.
3. Simon P., Gogotsi Y., Nature mater.,7, 845 (2008)