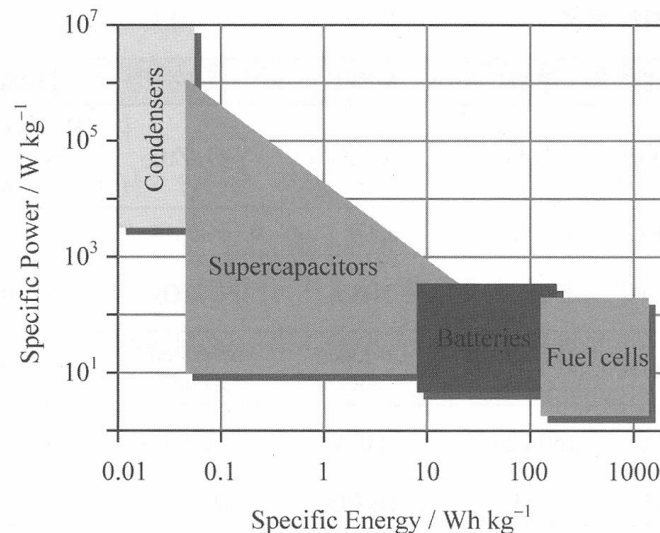


Electrochemical double-layer capacitors

1. Capacitor introduction
2. Electrical double-layer capacitance
3. I-V relationship for capacitors
4. Power and energy capabilities
5. Cell design, operation, performance
6. Pseudo-capacitance

Electrochemical double-layer capacitor (EDLC)

- Energy devices
- EDLCs complement batteries by providing greater power density at the expense of energy density
- EDLCs are often combined with batteries, fuel cells, and other devices in hybrid power systems
- Advantages of EDLCs: (i) high power density, (ii) long cycle life



Oh, ch.12

[그림 12-20] 콘덴서, 초고용량 커패시터, 전지, 연료 전지의 에너지 밀도와 출력 밀도를 비교한 라곤 도시

Ragone plots

-Power and energy are key design aims of an electrochemical system for energy storage and conversion

Power [W, kW], $P_{ave} = (1/t_d) \int IV(t)dt$

specific power [kW/kg],
specific energy [kWh/kg],
power density [kW/L],
energy density [kWh/L]

-Ragone plot:
trade-off between power and energy

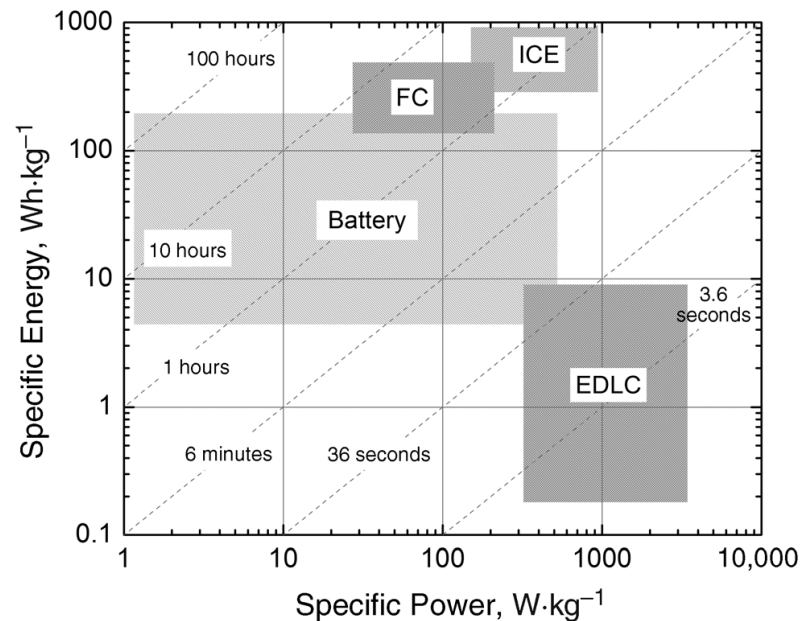


Figure 7.10 Ragone plot illustrating the strengths of different energy storage and conversion devices.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Capacitor introduction

-A **conventional electrostatic capacitor** consists of two conductors separated by a dielectric (electronic insulator)

$$\text{Capacitance, } C \text{ [F]} = Q/V$$

$$[\text{F}] = [\text{C/V}]$$

$$[\text{C} = \text{A} \cdot \text{s} = \text{FV}, \text{Ah} = 3600 \text{ FV}]$$

-differential capacitance, $C_d = dQ / dV$

-A conventional capacitor in vacuum, $C = \epsilon_0 A / d$

A: area, ϵ_0 : permittivity of free space, $8.8542 \times 10^{-12} \text{ Fm}^{-1}$

-(+) charged : anode, (-) charged : cathode

-vacuum \rightarrow dielectric

$$C = \epsilon A / d = \epsilon_r \epsilon_0 A / d$$

-dielectric constant, $\epsilon_r = \epsilon / \epsilon_0$

-capacitance \uparrow by area \uparrow , distance \downarrow

- A **electrolytic capacitor**: thin oxide layer as dielectric
- A **electrochemical double-layer capacitor (EDLC)**
- total capacitance in parallel, $C = C_1 + C_2 + C_3 \dots$
- total capacitance in series, $1/C = 1/C_1 + 1/C_2 + 1/C_3 \dots$

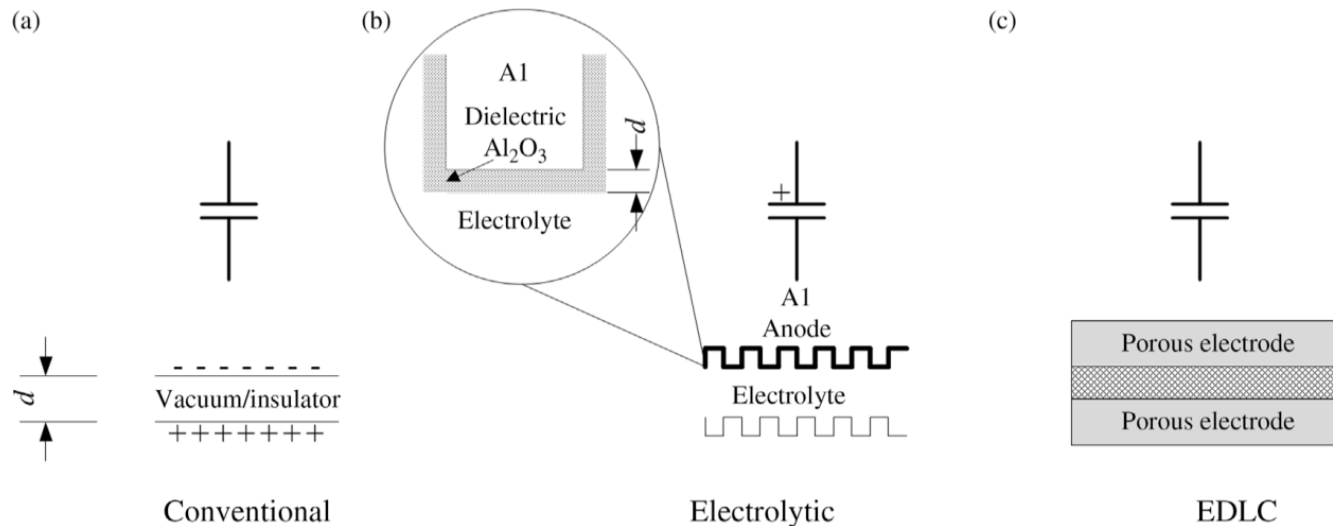
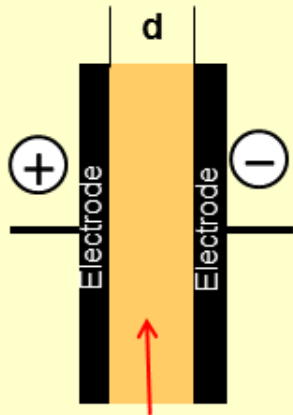


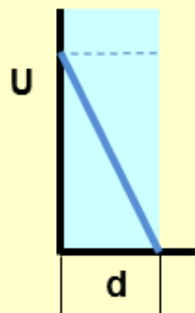
Figure 11.1 Types of capacitors and electrical symbols. (a) Conventional or electrostatic. (b) Electrolytic. (c) EDLC. Please note that, as discussed in the text, the electrical symbols do not accurately reflect the physics in Electrolytic capacitors and EDLCs—both of these have two capacitors in series, one for each electrode.

Fixed capacitors, charge storage principles

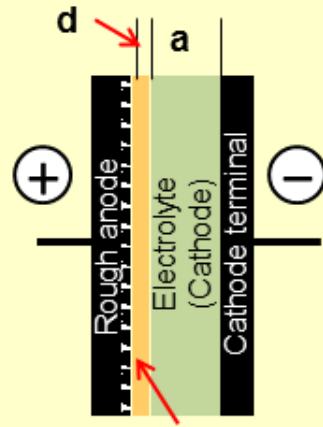
**Ceramic-,
Film capacitors
etc.**



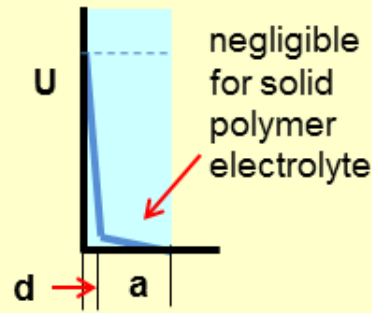
Ceramic, Film
(dielectric)
electrostatic storage



**Electrolytic
capacitors**

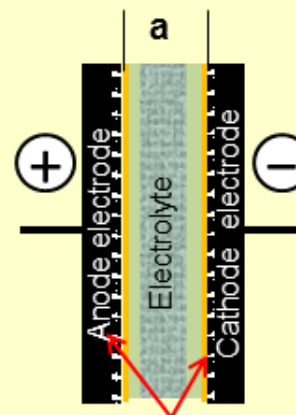


Oxide layer
(dielectric)
electrostatic storage



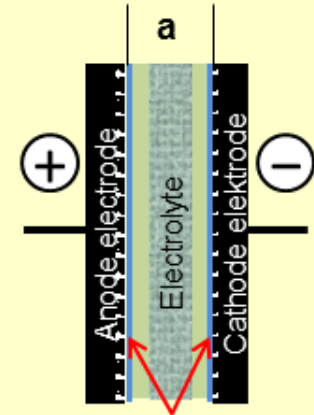
**Supercapacitors
(Electro-chemical capacitors)**

**Double-layer
capacitors**

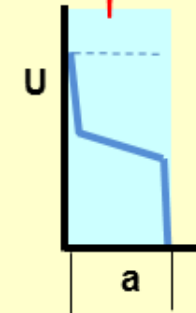


Helmholtz layers
electrostatic storage

**Pseudo-
capacitors**



Charge transfer,
redox reactions
electrochemical
storage



전기화학 용어와 단위

용어

단위

Current (I)	Ampere (A)
Current density (i)	Ampere per m ² (A/m ²)
Charge (q)	Coulomb (C = As)
Charge density (ρ)	Coulomb per m ³ (C/m ³)
Potential (ϕ)	Volt (V = J/C)
Field strength (X)	Volt per meter (V/m)
Conductivity (κ)	Siemens per meter (S/m)
Resistance (R)	Ohm (Ω = 1/S = V/A)
Conductance (G)	Siemens (S = A/V)
Permittivity (ϵ)	Farad per meter (F/m = C/Vm)
Energy (w)	Joule (J = VC)
Power	Watt (W = J/s = AV)
Capacitance (C)	Farad (F = s/ Ω = Ss), F = C/V

Capacitance

parallel conducting plate separated by a narrow gap containing air or insulator

$$\int I dt = Q \propto \Delta E$$

$$Q = -C\Delta E$$

C; capacitance (unit; farads (F) = C/V)

$$C = -Q/\Delta E = \epsilon A/L$$

A; cross-section area of the gap, L; width, ϵ ; permittivity of the insulator

- Relative permittivity (ϵ_r) or dielectric constant

air: ~ 1

water: 78 \rightarrow Coulomb interaction energy is reduced by two orders of magnitudes from its vacuum value

polar molecules: $\epsilon_r \uparrow$

refractive index: $n_r = \epsilon_r^{1/2}$ at the frequency

Capacitor; $\text{---} | | \text{---}$; current integrator

Permittivity of various materials

Material	$10^{12} \epsilon/\text{Fm}^{-1}$	Material	$10^{12} \epsilon/\text{Fm}^{-1}$
vacuum (ϵ_0)	8.85419	Neoprene	58
N ₂ (g)	8.85905	ClC ₂ H ₄ Cl(l)	91.7
Teflon(s), (CF ₂) _n	18	CH ₃ OH(l)	288.9
CCl ₄ (l)	19.7	C ₆ H ₅ NO ₂ (l)	308.3
Polyethene (s)	20	CH ₃ CN(l)	332
Mylar (s)	28	H ₂ O(l)	695.4
SiO ₂ (s)	38.1	HCONH ₂ (l)	933
Typical glass (s)	44	TiO ₂ (s)	≤1500
C ₆ H ₅ Cl(l)	49.8	BaTiO ₃ (s)	≤110000

ϵ/ϵ_0 ; relative permittivity or dielectric constant

mylar; poly(ethylene glycol terephthalate), (CH₂OOCC₆H₄COOCH₂)_n

Liquid > solid: large capacitance in electrochemical capacitor (supercapacitor)

Electrical double-layer (전기이중층) capacitance

Inner layer (compact, Helmholtz, Stern):

solvent, specifically adsorbed species

Outer Helmholtz plane (OHP): solvated ions

Diffusion layer of double layer: extends from OHP to the bulk
($\sim 100 \text{ \AA}$ in $>10^{-2} \text{ M}$)

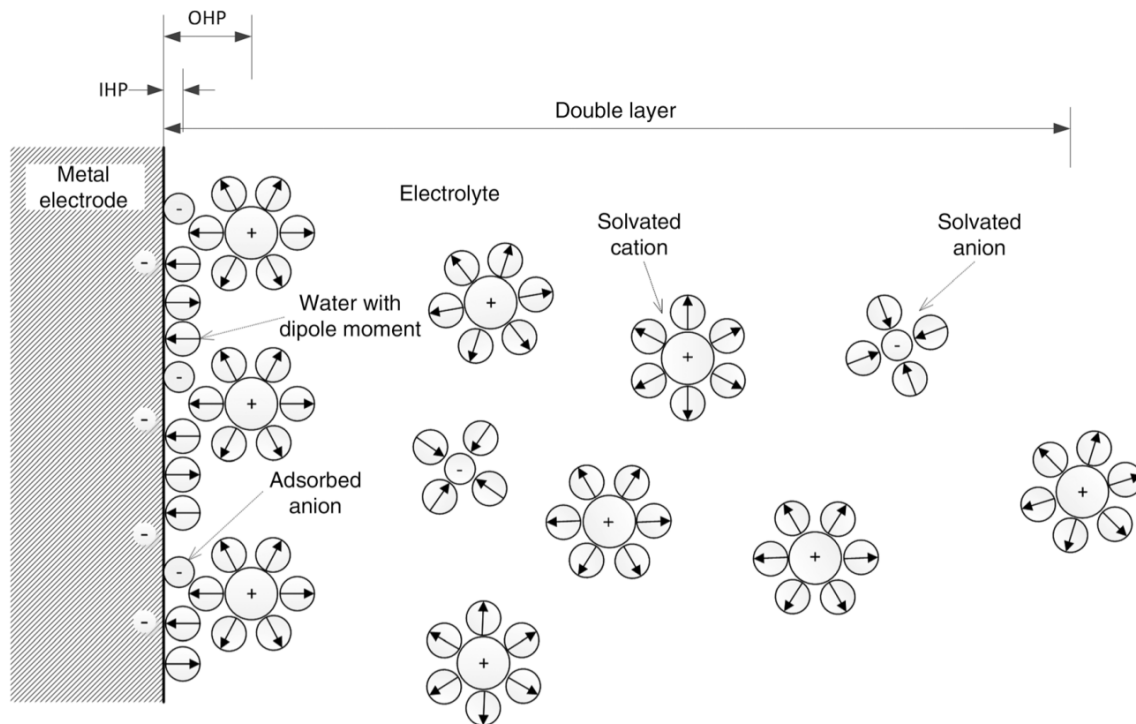


Figure 11.2 Structure of the electrical double layer.

Capacitance and charge of an electrode

- Interface = capacitor (two metal sheets separated by a dielectric material)

$$q/E = C$$

q: charge stored on the capacitor (C, coulomb)

E: potential across the capacitor (V), C: capacitance (F, farad)

- During this charging process, a current ("charging current") will flow

- 2 V battery across 10 μF capacitor

→ current will flow until 20 μC accumulated

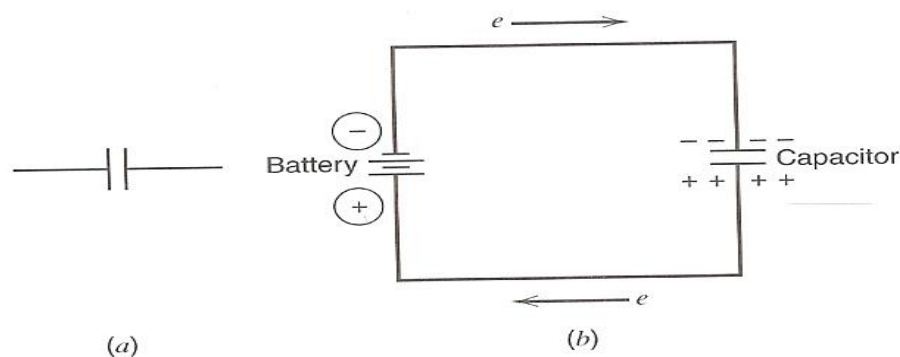
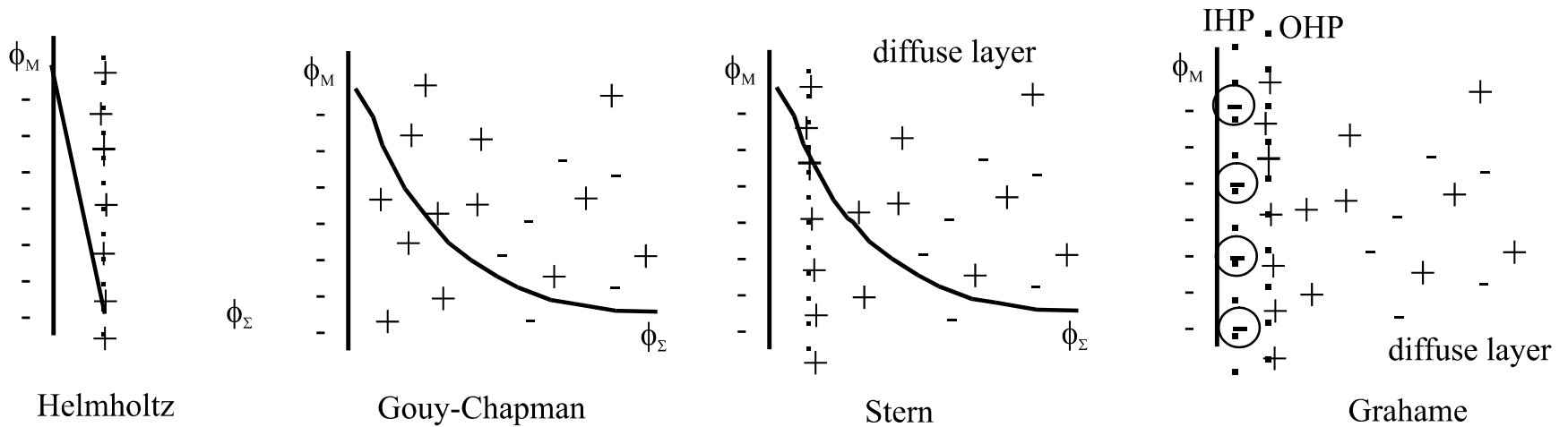


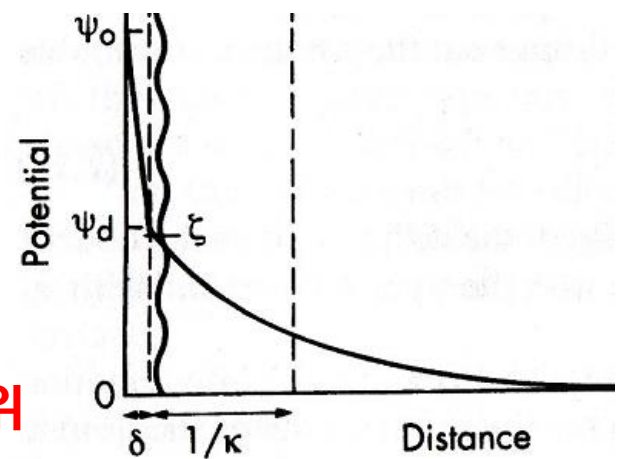
Figure 1.2.1 (a) A capacitor. (b) Charging a capacitor with a battery.



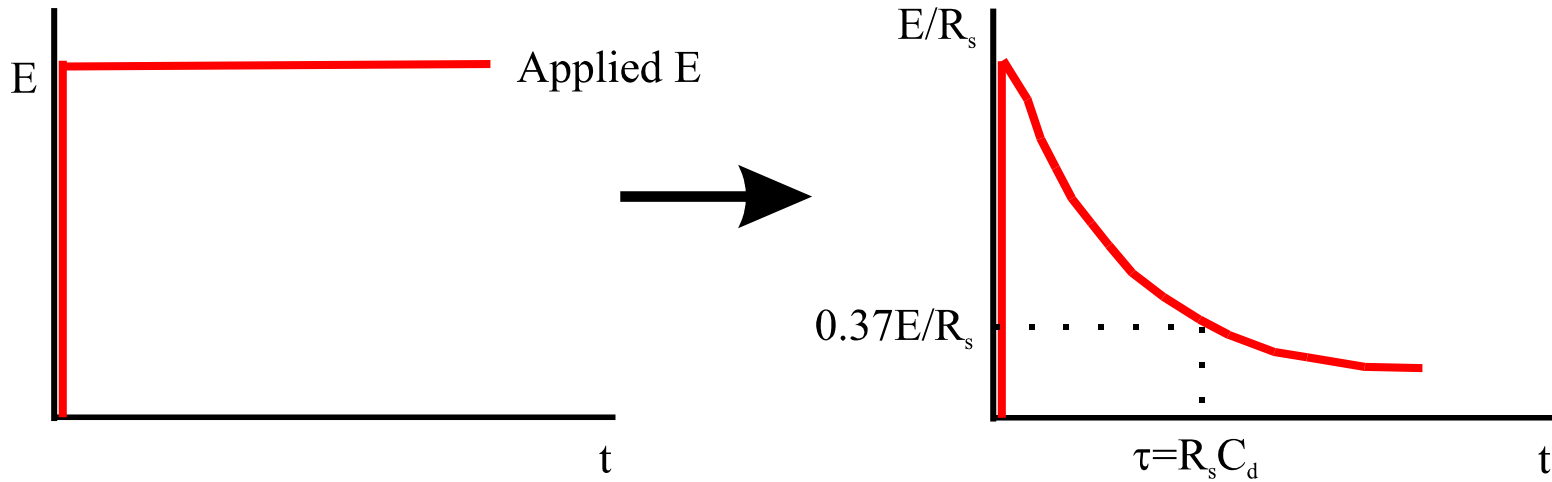
Stern model

The potential at the shear plane is called **electrokinetic** or **zeta (ζ) potential**, which can be measured experimentally

제타전위



Applying potential to electrode:
→ current for charging the double layer capacitance



e.g.,) $R_s = 1 \Omega$, $C_d = 20 \mu F$, $\tau = 20 \mu sec$ → double layer charging is 95 % complete in $60 \mu sec$

Double layer charging process: “**non-faradaic process**”
(no oxidation/reduction, no charge transfer)

EDLC, or pseudocapacitor, supercapacitor, ultracapacitor

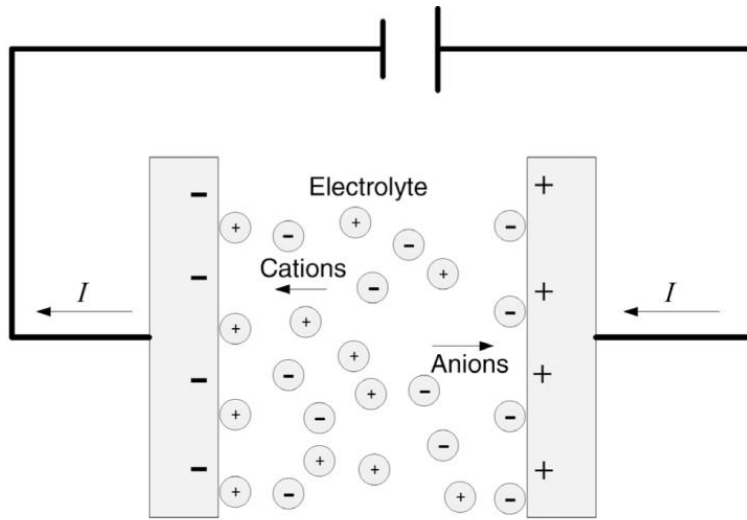
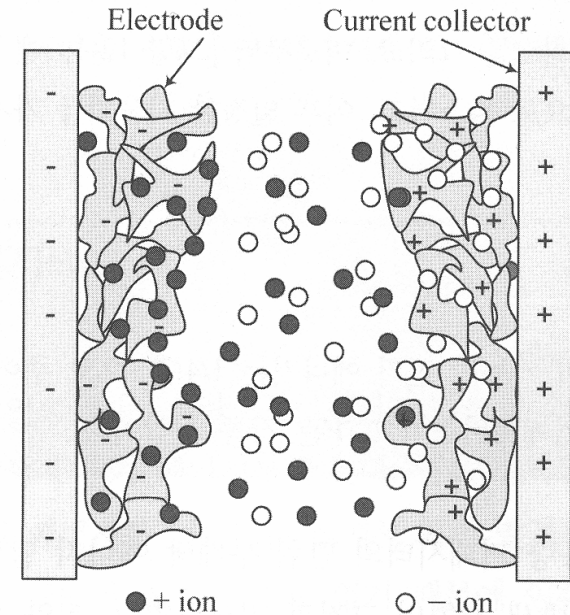


Figure 11.3 Charging of an EDLC.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering



1림 12-18] 대칭형 전기 이중층 커패시터(EDLC)의 구성

Oh, ch.12

Current-voltage relationship for capacitors

$$I = C(dV/dt)$$

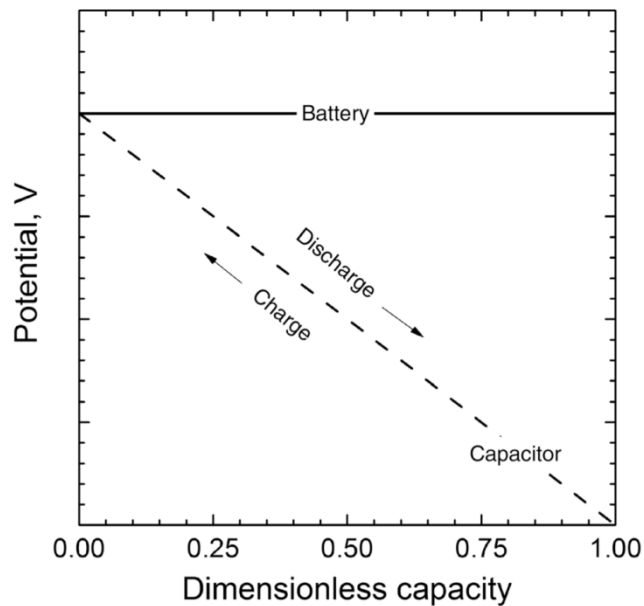
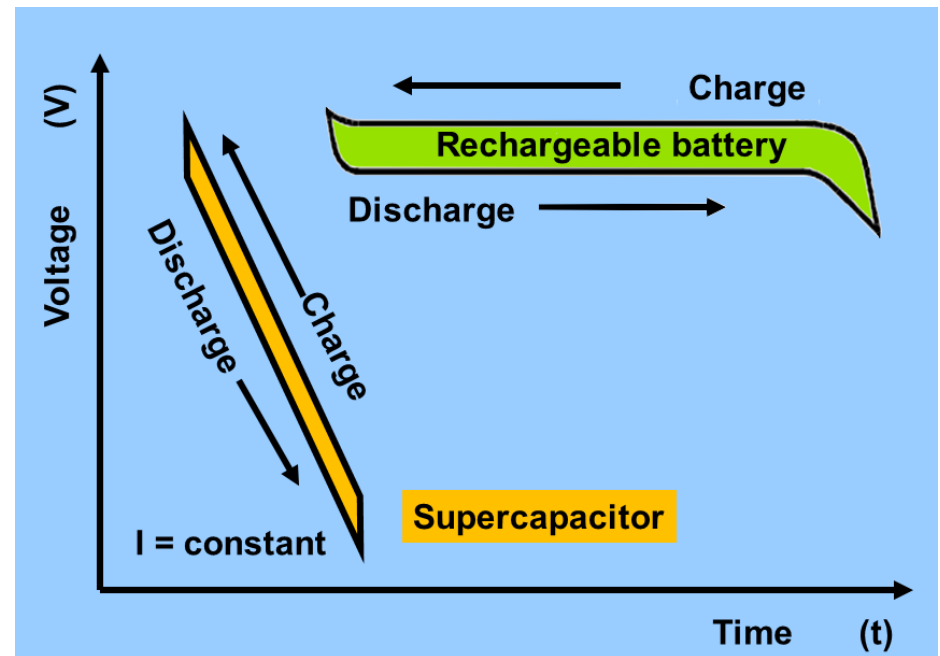


Figure 11.8 Comparison of ideal battery with an ideal capacitor.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering



<https://upload.wikimedia.org/wikipedia/commons/e/ed/Charge-Discharge-Supercap-vs-Battery.png>

Power and energy capabilities

The change in energy associated with a change in capacitor voltage,
 $dE = VdQ = CVdV$

The total energy stored in the capacitor,
 $E = \int dE = C \int VdV = CV^2/2 = QV/2$

where we have assumed that C is constant
 $[F] = [JV^{-2}]$ or $[CV^{-1}]$

→ we estimate the amount of energy stored in different types of capacitors

Illustration 11.8

The power is energy per unit time,

$$P = IV$$

The power will be a maximum for the initial discharge of a capacitor

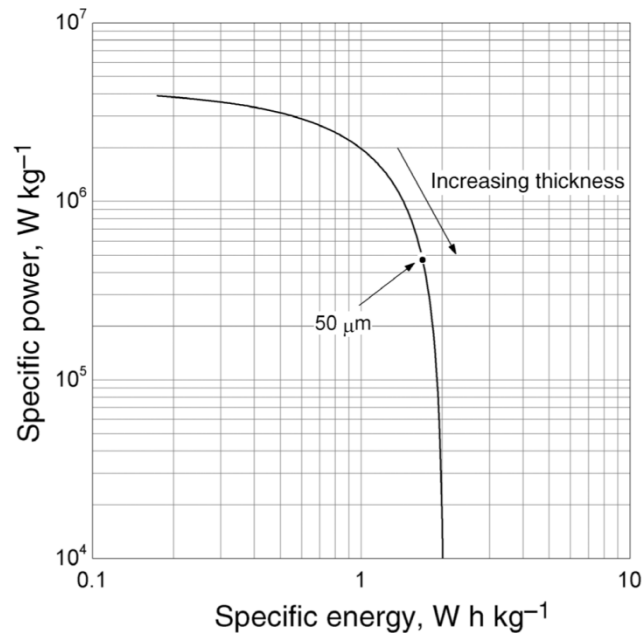


Figure 11.16 Comparison of maximum specific power and specific energy. The parameters are from Illustration 11.6 and the thickness of electrode varied.

Cell design

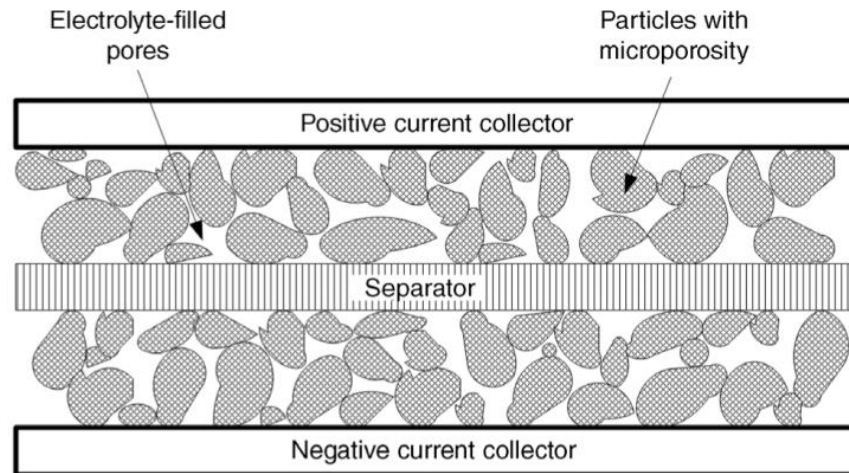


Figure 11.18 Construction of a typical EDLC. Notice the similarities of the cell sandwich with that of batteries and fuel cells.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.
© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Pseudo-capacitance

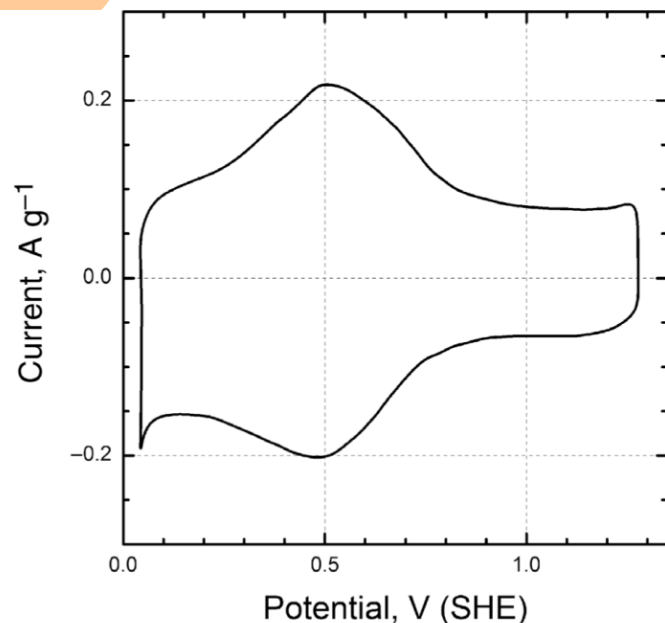


Figure 11.21 Cyclic voltammetry behavior of Vulcan XC-72 in phosphoric acid after oxidation. (Adapted from K. Kinoshita and J.A. S. Bett (1973) *Carbon*, **11**, 403.)

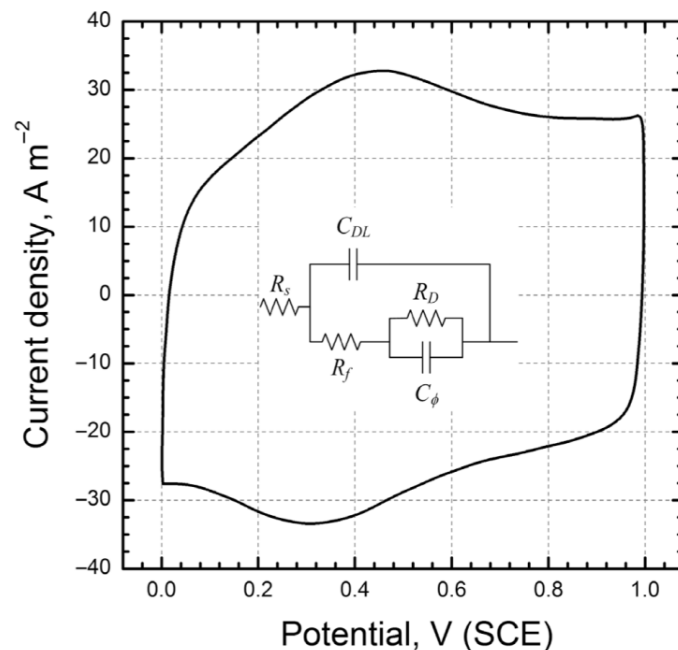


Figure 11.22 Cyclic voltammetry behavior of RuO₂. The scan rate is 20 mV·s⁻¹. Common equivalent circuit for pseudo-capacitor is also shown. *Source:* Adapted from Kim 2001.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc. © 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

© 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc. © 2018 Thomas F. Fuller and John N. Harb. Published 2018 by John Wiley & Sons, Inc.

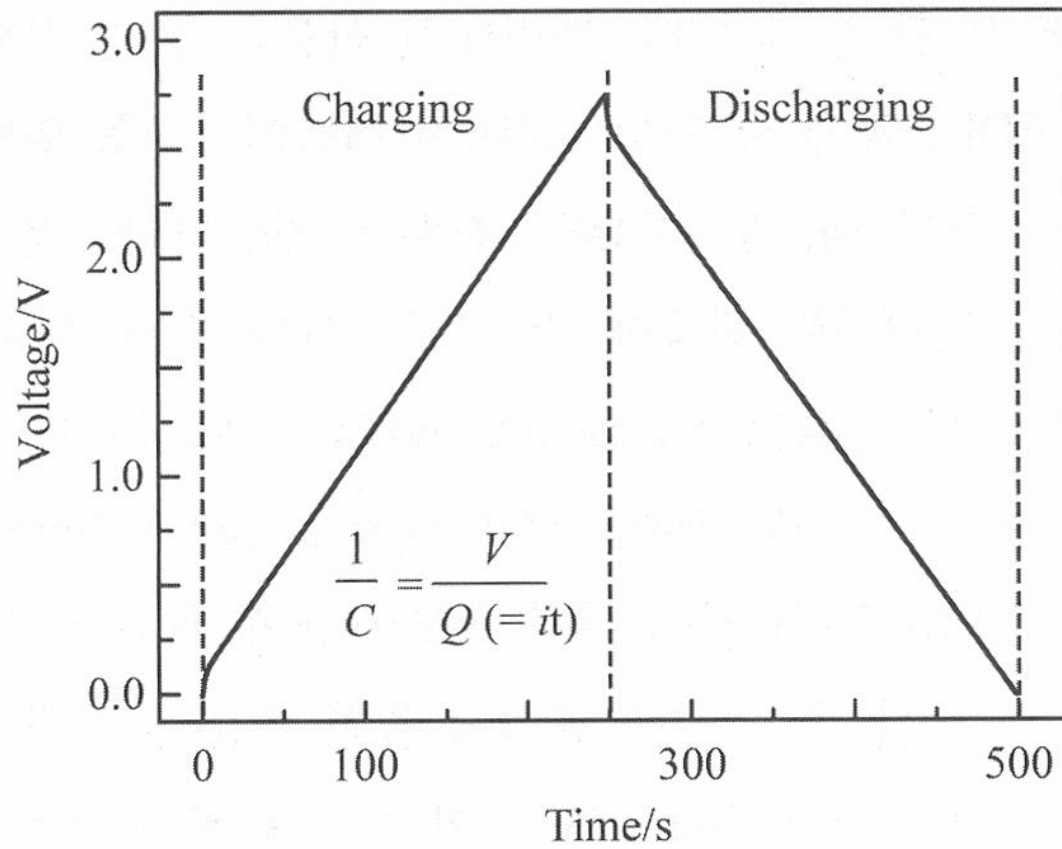
Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Faradaic reaction, $\text{RuO}_x(\text{OH})_y + \text{H}^+ + \text{e}^- \leftrightarrow \text{RuO}_{x-1}(\text{OH})_{y+1}$

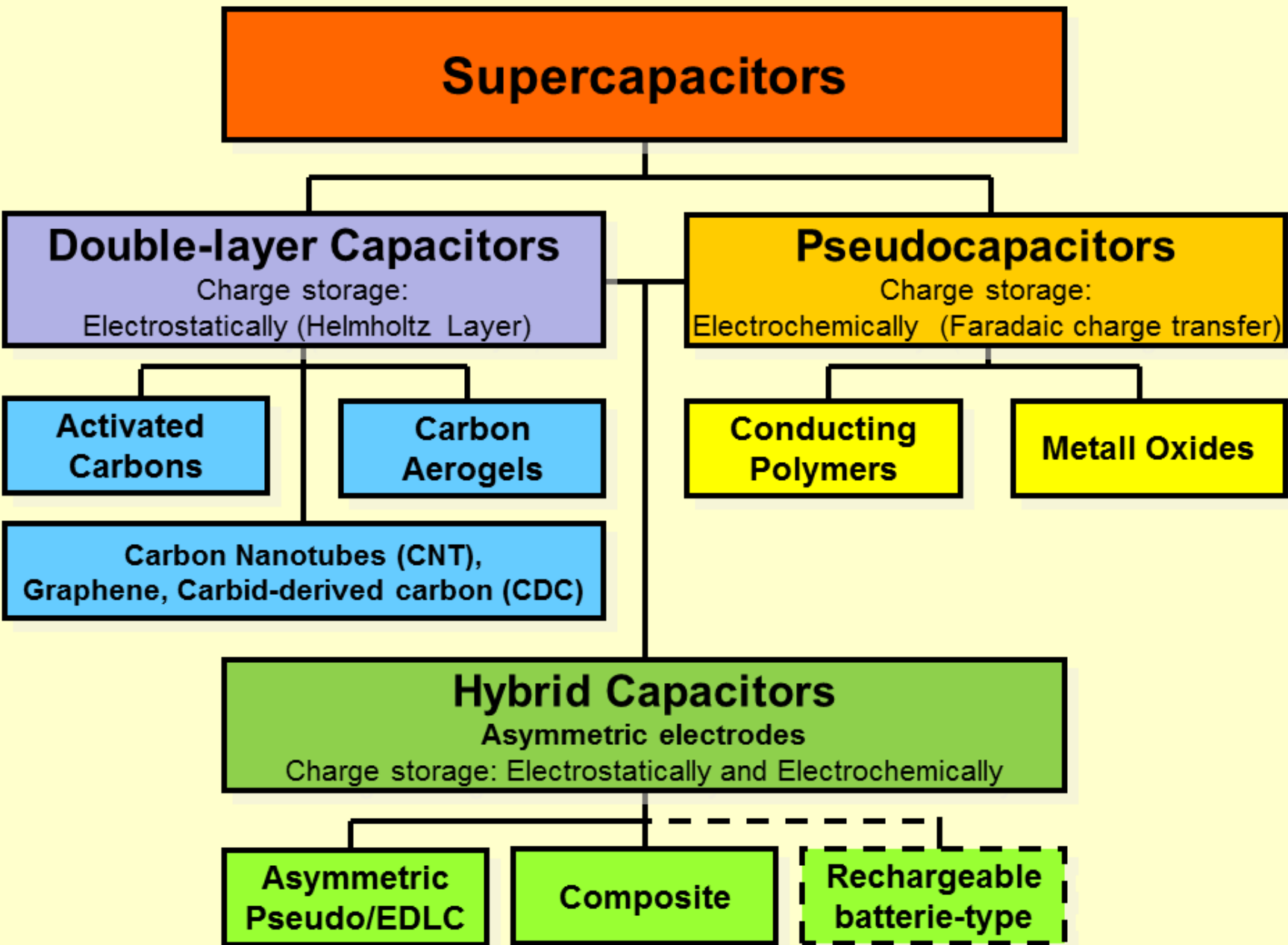
→ high surface area is critical for high energy storage

Capacitance, $C = (\text{d}q/\text{d}t) / (\text{d}V/\text{d}t) \sim i_{\text{avg}} / v$

Capacitance for pseudocapacitor: 5 ~ 10 F/m² (cf. CDL ~ 0.25 F/m²)



[그림 12-19] 전기 이중층 커패시터(EDLC)의 정전류 충방전 곡선



Performance parameters of supercapacitors compared with electrolytic capacitors and lithium-ion batteries

Parameter	Aluminium electrolytic capacitors	— Supercapacitors —			Lithium-ion batteries
		Double-layer capacitors	Pseudo-capacitors	Hybrid (Li-Ion)	
Temperature, (°C)	−40 ... +125 °C	−40 ... +70 °C	−20 ... +70 °C	−20 ... +70 °C	−20 ... +60 °C
Max charge, (V)	4 ... 630 V	1.2 ... 3.3 V	2.2 ... 3.3 V	2.2 ... 3.8 V	2.5 ... 4.2 V
Recharge cycles, thousands (k)	< unlimited	100k ... 1000k	100k ... 1000k	20k ... 100k	0.5k ... 10k
<u>Capacitance</u> , (F)	≤ 2.7 F	0.1 ... 470 F	100 ... 12000 F	300 ... 3300 F	—
<u>Specific energy</u> , (Wh/kg)	0.01 ... 0.3 Wh/kg	1.5 ... 3.9 Wh/kg	4 ... 9 Wh/kg	10 ... 15 Wh/kg	100 ... 265 Wh/kg
<u>Specific power</u> , (W/g)	> 100 W/g	2 ... 10 W/g	3 ... 10 W/g	3 ... 14 W/g	0.3 ... 1.5 W/g
Self-discharge time at room T	short (days)	middle (weeks)	middle (weeks)	long (month)	long (month)
Efficiency (%)	99%	95%	95%	90%	90%
Working life at room T (y)	> 20 y	5 ... 10 y	5 ... 10 y	5 ... 10 y	3 ... 5 y