Lecture Note #11 (Spring, 2022)

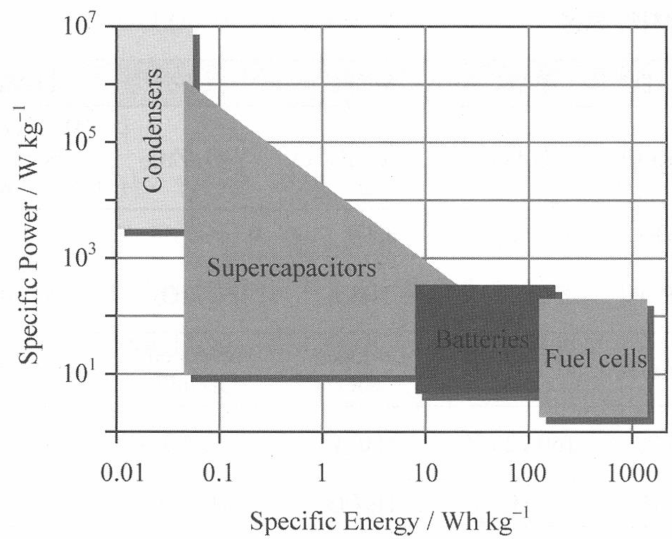
Electrochemical double-layer capacitors

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

Fuller & Harb (textbook), ch.11, Bard (ref.), ch.1

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



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

Oh, ch.12

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

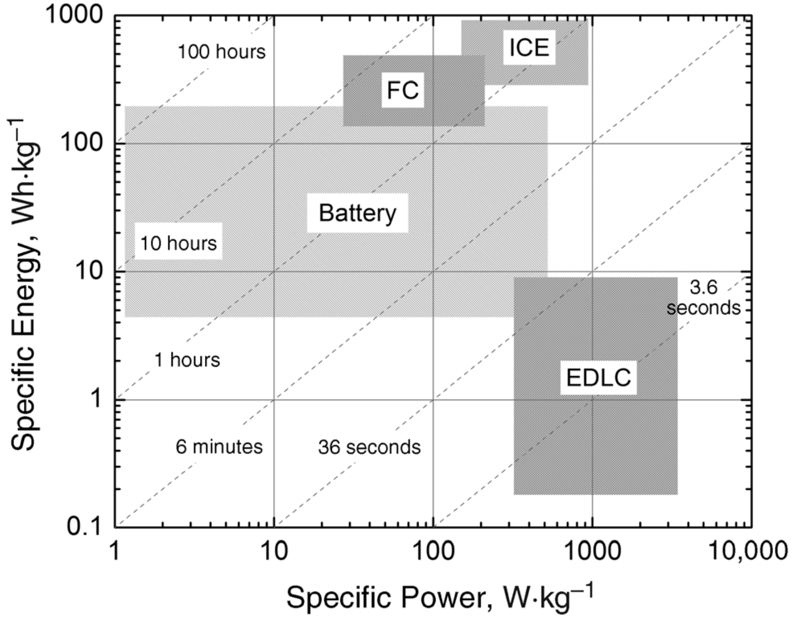


Figure 7.10 Ragone plot illustrating the strengths of different energy storage and conversion devices.

Capacitor introduction

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

Capacitance, C [F] = Q/V

[F] = [C/V]

[C = A·s = FV, Ah = 3600 FV]

-differential capacitance, $C_d = dQ / dV$

-A conventional capacitor in vacuum, $C = \varepsilon_0 A / d$

A: area, ε_0: permittivity of free space, 8.8542×10^{-12} Fm^{-1}

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

-vacuum → dielectric

$$C = \varepsilon A / d = \varepsilon_r \varepsilon_0 A / d$$

-dielectric constant, $\varepsilon_r = \varepsilon / \varepsilon_0$

-capacitance↑ by area↑, distance↓

-A electrolytic capacitor: thin oxide layer as dielectric

-A electrochemical double-layer capacitor (EDLC)

-total capacitance in parallel, $C = C_1 + C_2 + C_3 \ldots.$
-total capacitance in series, $1/C = 1/C_1 + 1/C_2 + 1/C_3 \ldots.$

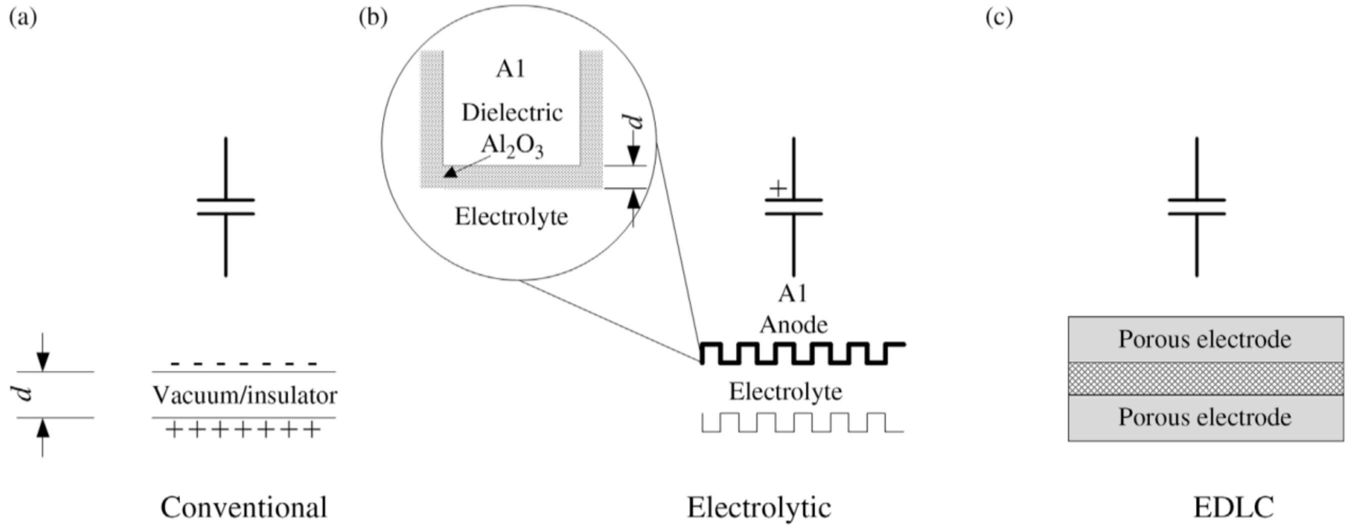
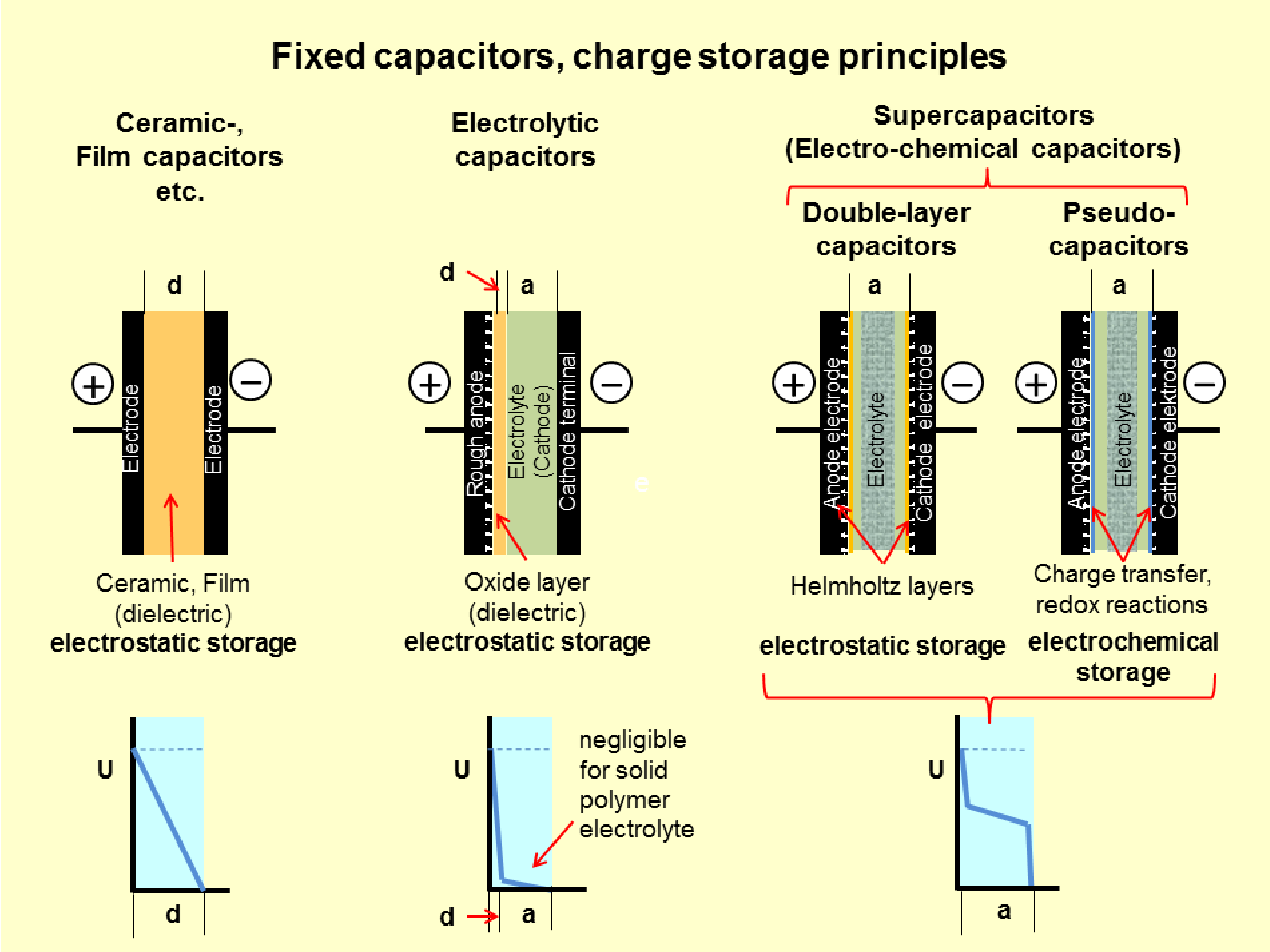


Figure 11.1 Types of capacitors and electrical symbols. (a) Conventional or electrostatic. (b) Electrolytic. (c) EDLC. Please note that, as discussed in the text, the electrical symbols do not accurately reflect the physics in Electrolytic capacitors and EDLCs—both of these have two capacitors in series,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

Illustration 11.1



https://en.wikipedia.org/wiki/Supercapacitor

Term & unit in electrochemistry

Term	Unit
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

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

$$\mathbf{Q = -C\Delta E}$$

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

$$\mathbf{C = -Q/\Delta E = \varepsilon A/L}$$

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

Capacitor; —| |— ; current integrator

Permittivity of various materials

Material	10^{12} ε/Fm^{-1}	Material	10^{12} ε/Fm^{-1}
vacuum (ε_0)	8.85419	Neoprene	58
N_2(g)	8.85905	ClC_2H_4Cl(l)	91.7
Teflon(s), $(CF_2)_n$	18	CH_3OH(l)	288.9
CCl_4(l)	19.7	$C_6H_5NO_2$(l)	308.3
Polyethene (s)	20	CH_3CN(l)	332
Mylar (s)	28	H_2O(l)	695.4
SiO_2(s)	38.1	$HCONH_2$(l)	933
Typical glass (s)	44	TiO_2(s)	≤1500
C_6H_5Cl(l)	49.8	$BaTiO_3$(s)	≤110000

$\varepsilon/\varepsilon_0$; relative permittivity or dielectric constant
mylar; poly(ethylene glycol terephthalate), $(CH_2OOCC_6H_4COOCH_2)_n$
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
(~100 Å in >10^{-2} M)

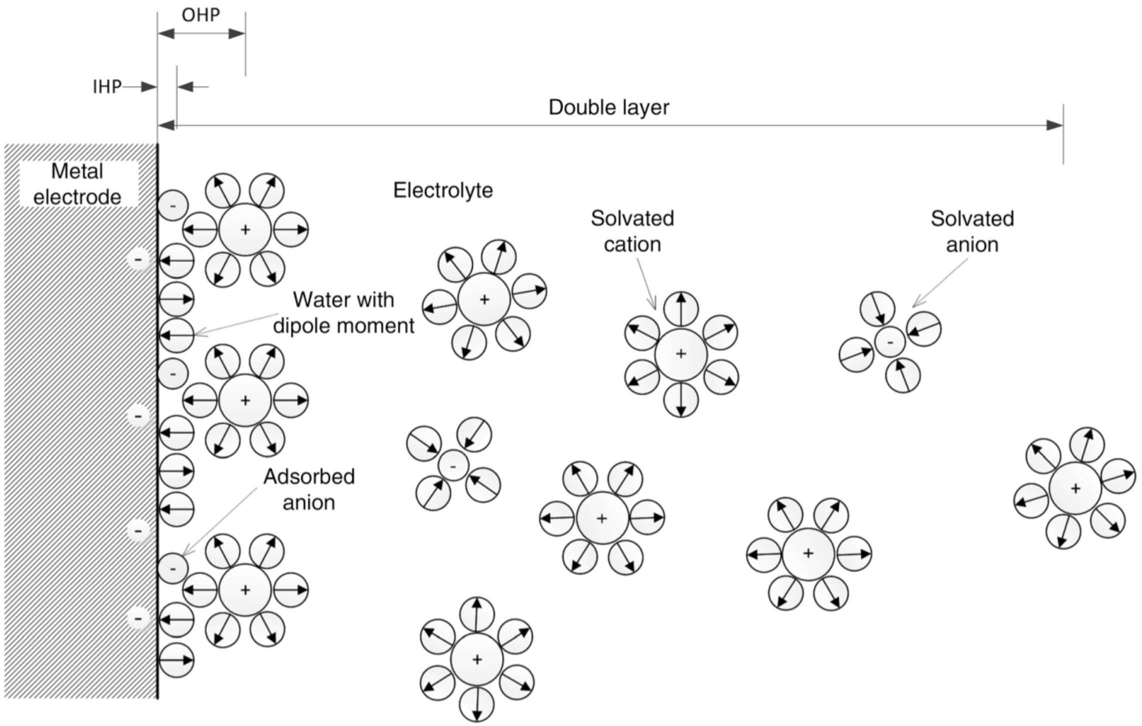


Figure 11.2 Structure of the electrical double layer.

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 20μC accumulated

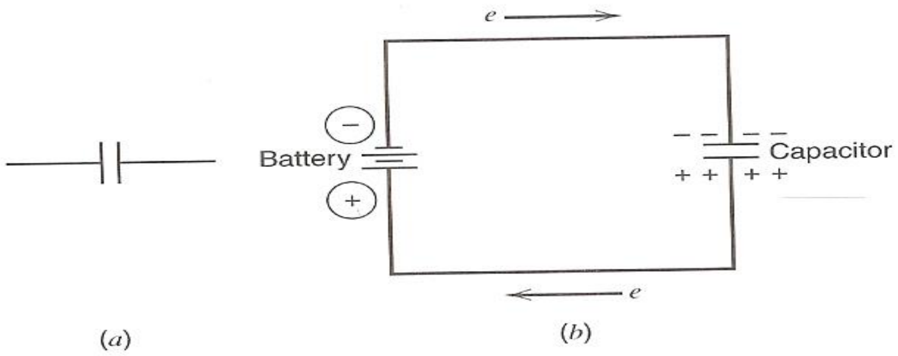
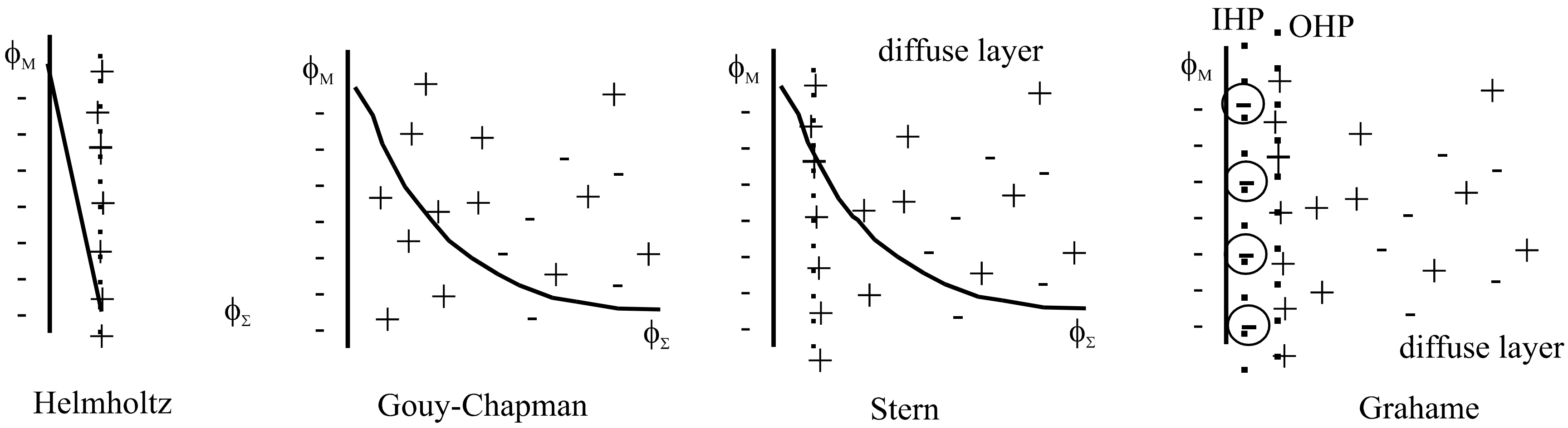


Figure 1.2.1 (*a*) A capacitor. (*b*) Charging a capacitor with a battery.

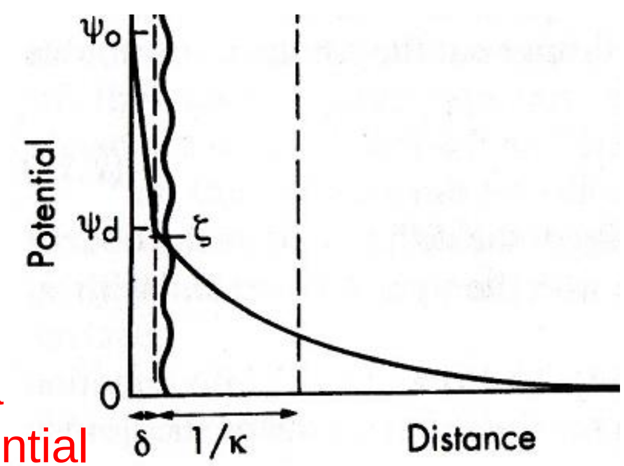
Bard, ch.1



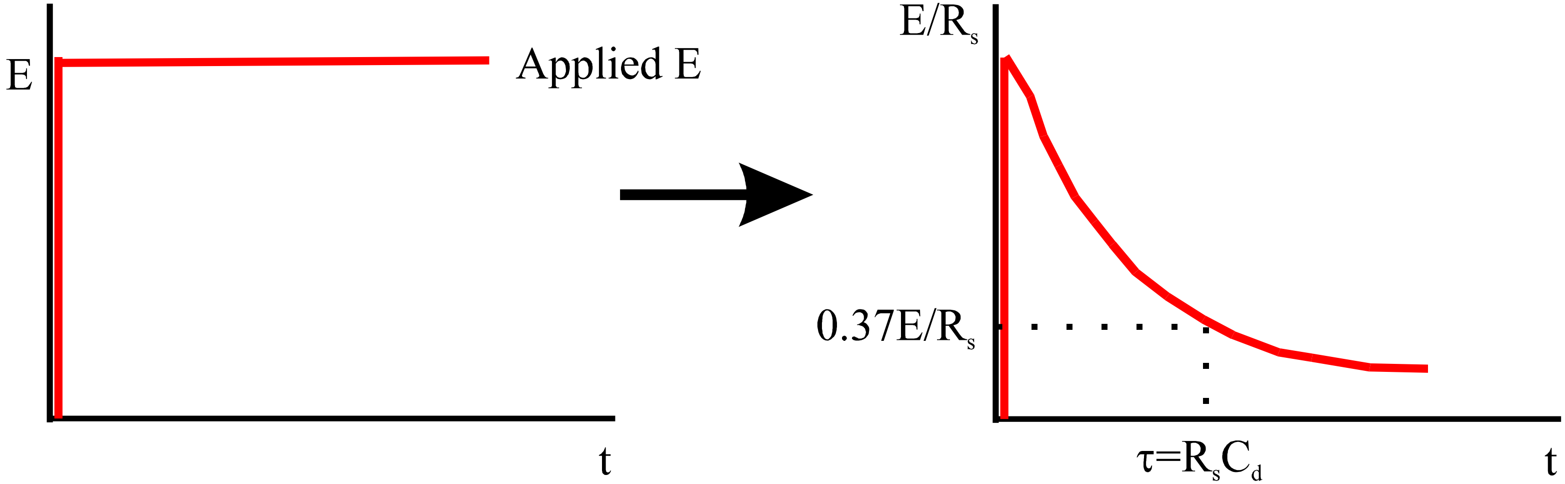
Stern model

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

Zeta potential



Applying potential to electrode:
$\rightarrow$ current for charging the double layer capacitance



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

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

EDLC, or pseudocapacitor, supercapacitor, ultracapacitor

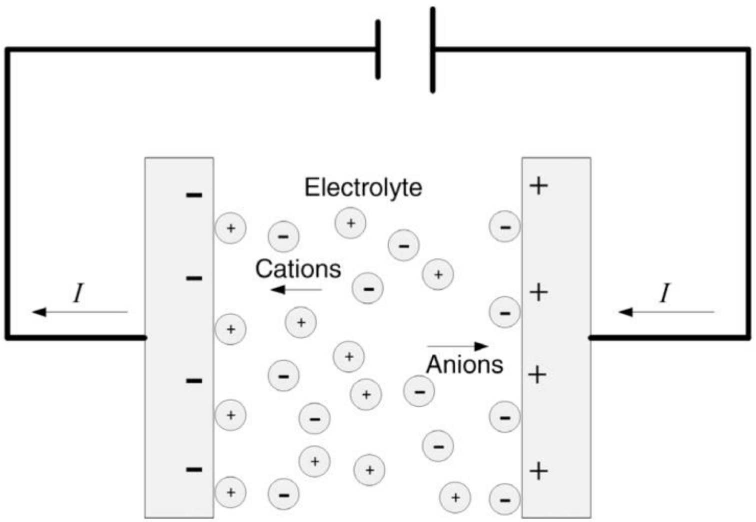


Figure 11.3 Charging of an EDLC.

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

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

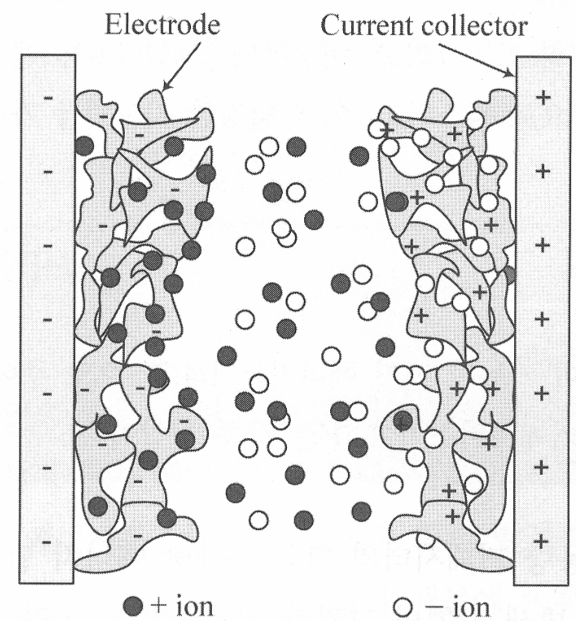


그림 12–18] 대칭형 전기 이중층 커패시터(EDLC)의 구성

Oh, ch.12

Illustration 11.2

Current-voltage relationship for capacitors

I = C(dV/dt)

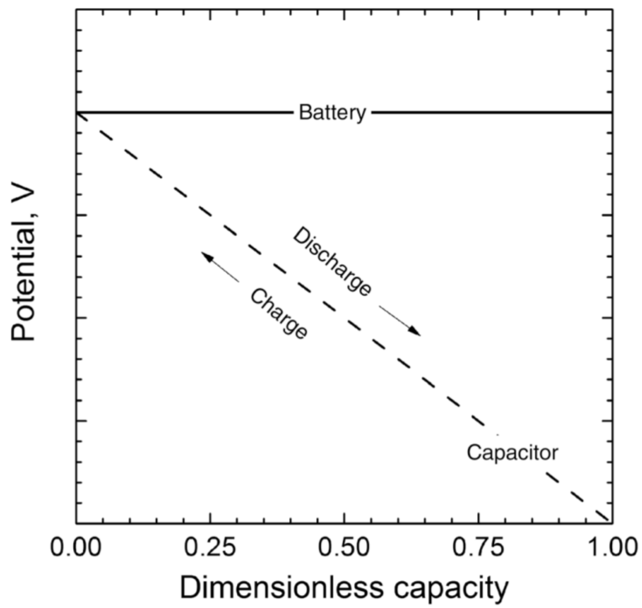


Figure 11.8 Comparison of ideal battery with an ideal capacitor.

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

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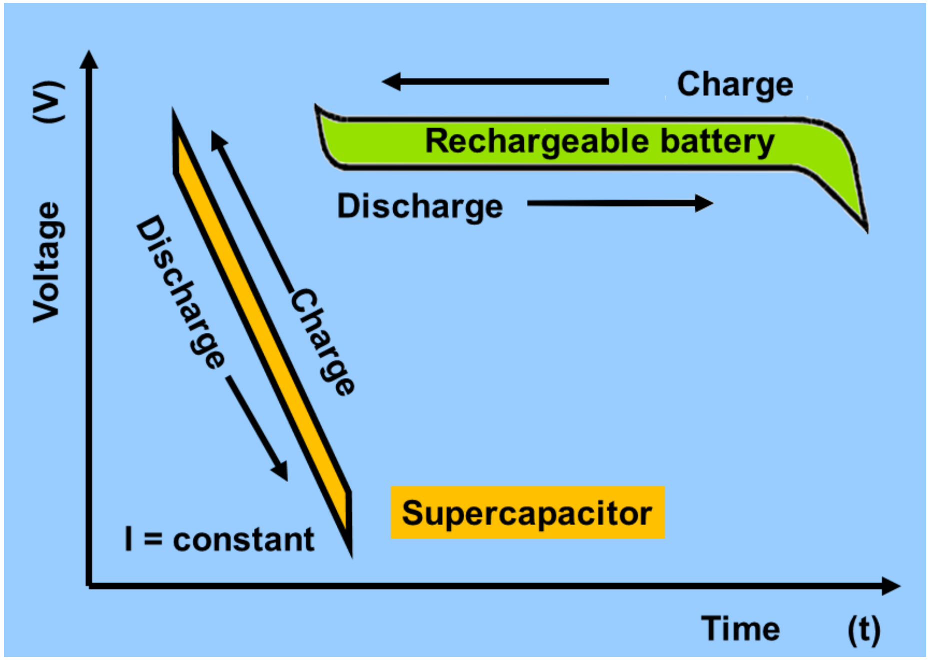

https://upload.wikimedia.org/wikipedia/commons/e/ed/Charge-Discharge-Supercap-vs-Battery.png

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

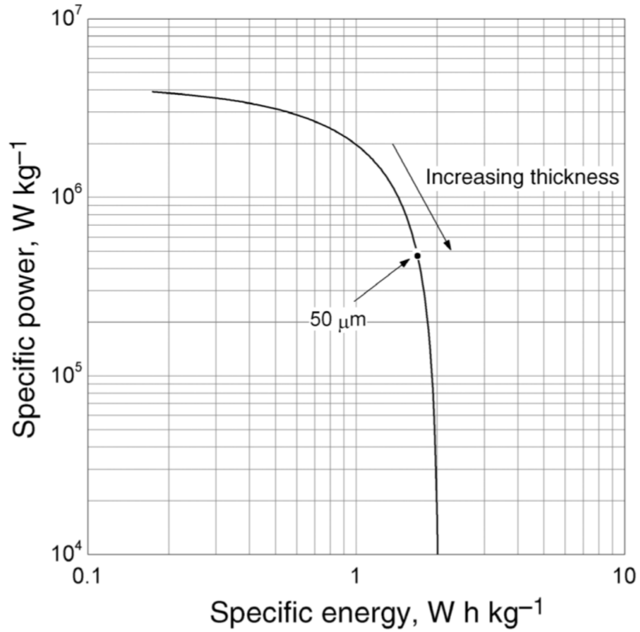

Figure 11.16 Comparison of maximum specific power and specific energy. The parameters are from Illustration 11.6 and the thickness of electrode varied.

For thicker electrode, lower rate capability, constant specific energy

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Cell design

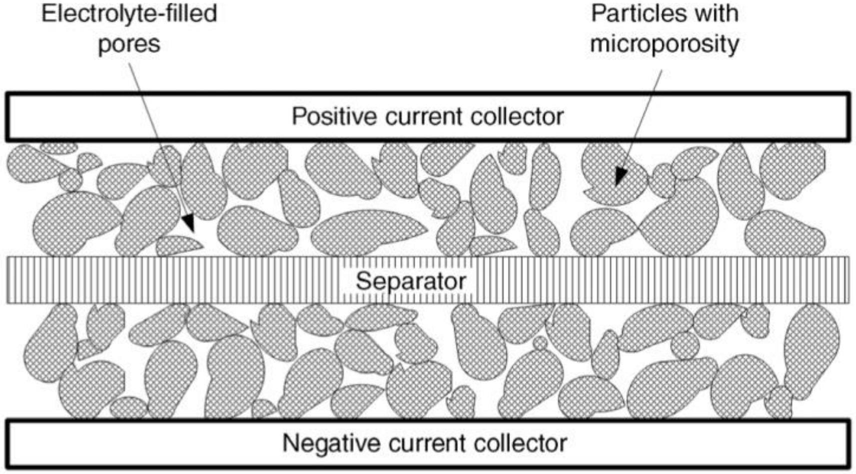

Figure 11.18 Construction of a typical EDLC. Notice the similarities of the cell sandwich with that of batteries and fuel cells.

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Pseudo-capacitance

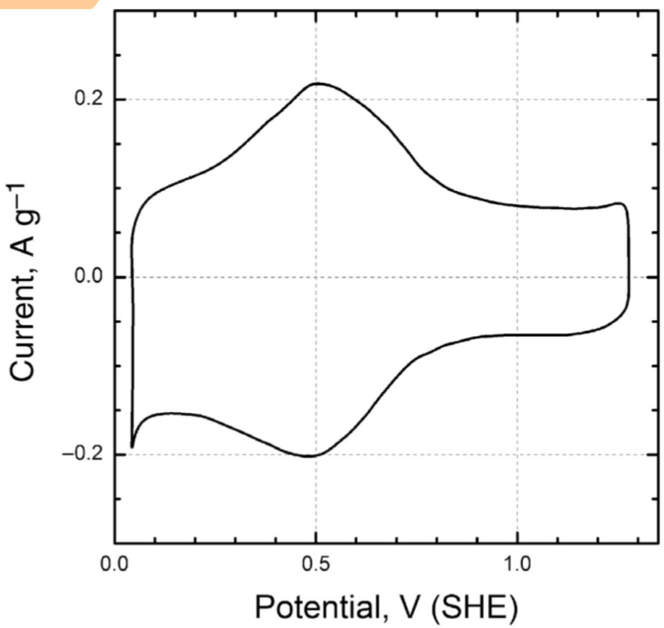

Figure 11.21 Cyclic voltammetry behavior of Vulcan XC-72 in phosphoric acid after oxidation. (Adapted from K. Kinoshita and J.A. S. Bett (1973) *Carbon*, **11**, 403.)

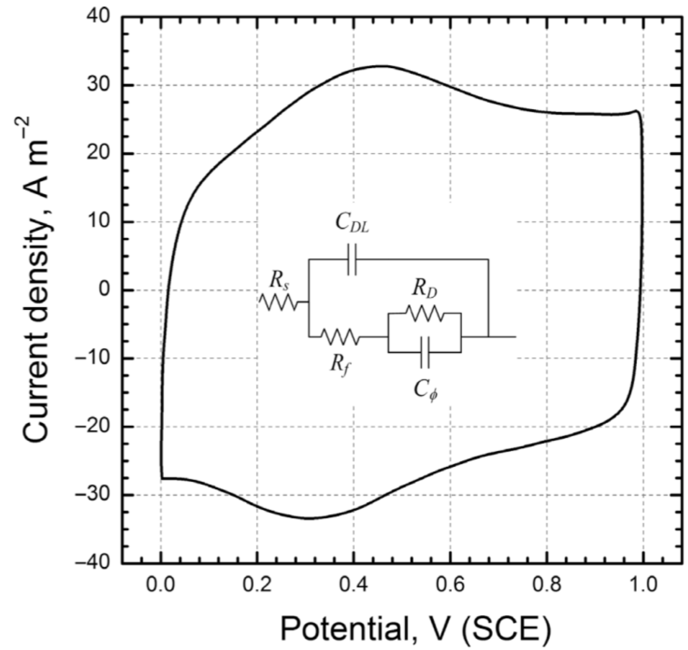

Figure 11.22 Cyclic voltammetry behavior of RuO_2. The scan rate is 20 $mV{\cdot}s^{-1}$. Common equivalent circuit for pseudo-capacitor is also shown. *Source:* Adapted from Kim 2001.

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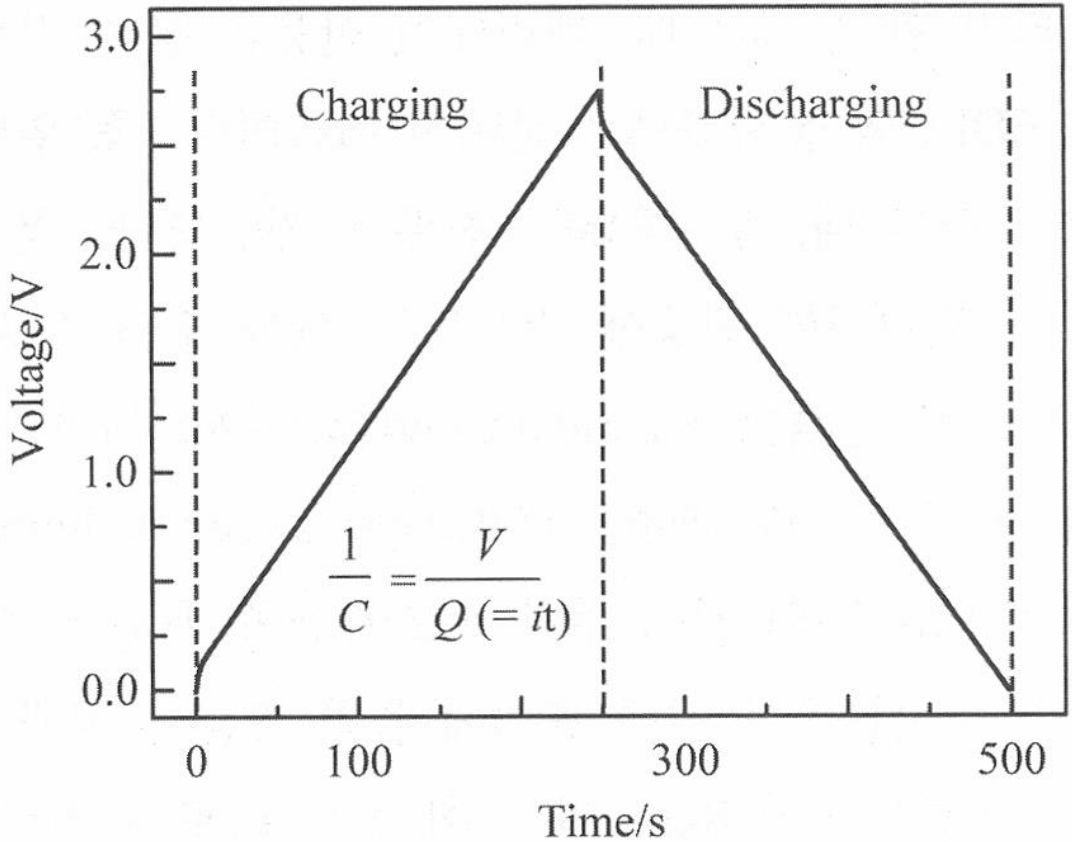
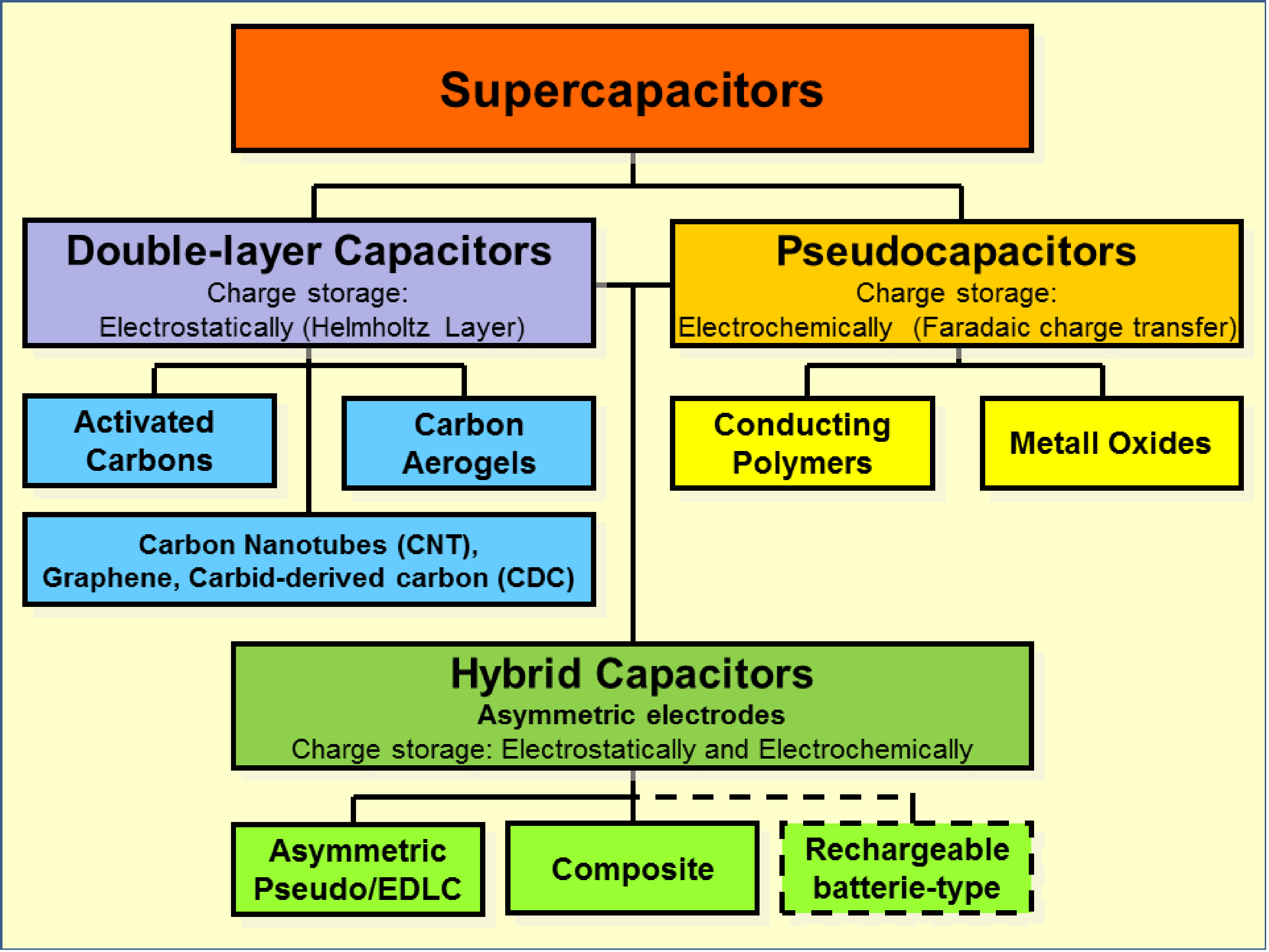
Faradaic reaction, $RuO_x(OH)_y + H^+ + e^- \leftrightarrow RuO_{x-1}(OH)_{y+1}$
→ high surface area is critical for high energy storage
Capacitance, $C = (dq/dt) / (dV/dt) \sim i_{avg} / v$
Capacitance for pseudocapacitor: 5 ~ 10 F/m^2 ((cf. C_{DL} ~ 0.25 F/m^2)

constant current



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

Oh, ch.12



https://en.wikipedia.org/wiki/Supercapacitor

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
Capacitance, (F)	≤ 2.7 F	0.1 ··· 470 F	100 ··· 12000 F	300 ··· 3300 F	—
Specific energy, (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
Specific power, (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

https://en.wikipedia.org/wiki/Supercapacitor