Supercapacitors
Technical and Physical Basics of EDLC

more than you expect

APEC 2019 in Anaheim
Capacitor Workshop PSMA

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Short Introduction of Today‘s Presenter

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Background:

- Experience in
  - application-oriented research
  - development of organic electronics,
  - polymer analysis
- Responsible for Supercapacitors

Agenda

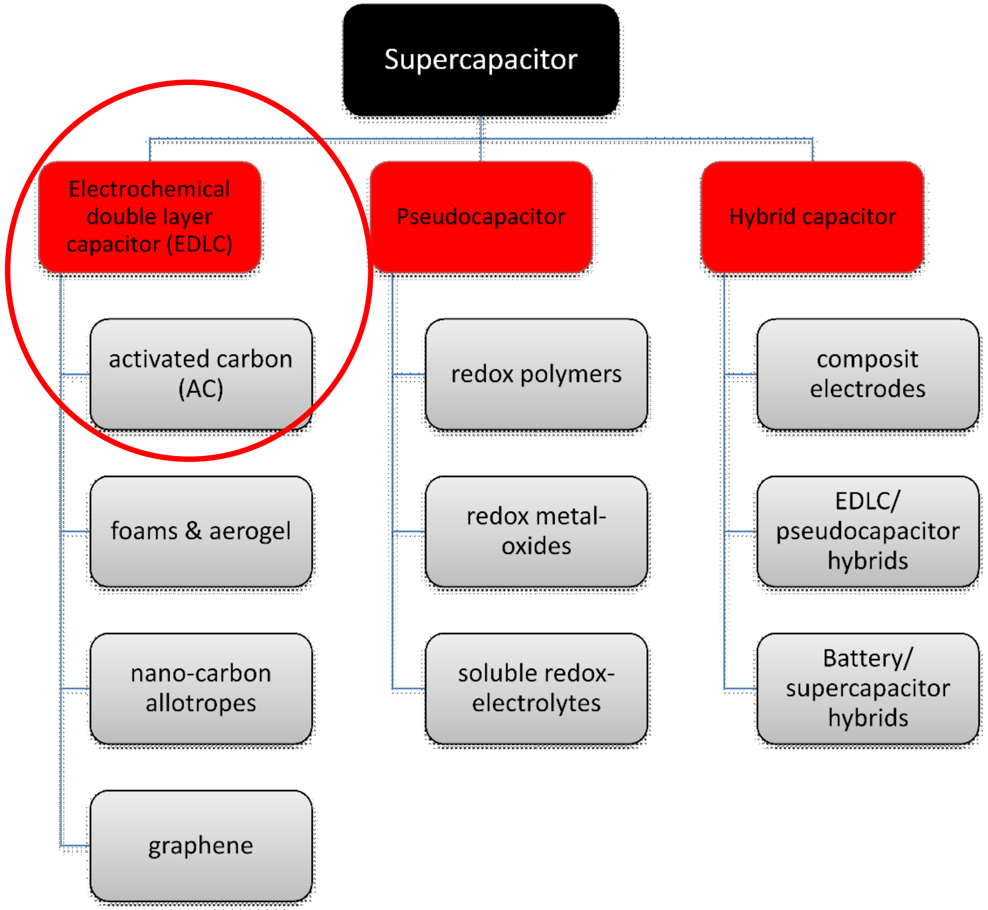
- Classification of Capacitors
- Physical Processes
- Model Parameters and Performance
- Charge, Discharge and frequency behavior
- Physical limitations of capacitance

Classification of Capacitors

- Tradename / Synonyms:

  - APowerCap,
  - BestCap,
  - BoostCap,
  - CAP-XX,
  - EVerCAP,
  - DynaCap,
  - Goldcap,
  - HY-CAP,
  - SuperCap,
  - PAS Capacitor,
  - PowerStor,
  - PseudoCap,
  - Ultracapacitor,
  - Ultracap,
  - ENYCAP,
  - ...

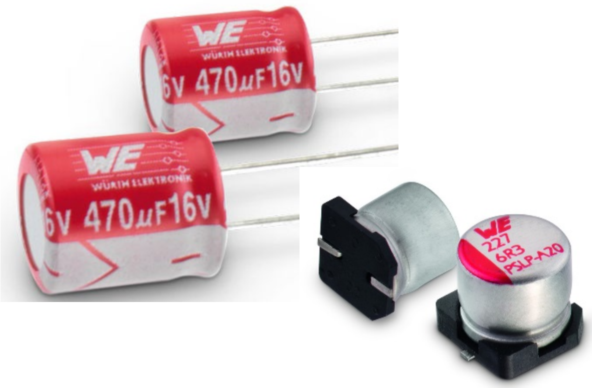
Classification of Capacitors



Types of Supercapacitors, based on design of electrodes:

- **Double-layer capacitors**
  - **Electrodes: carbon or carbon derivatives**
- **Pseudocapacitors**
  - **Electrodes: oxides or conducting polymers (high faradaic pseudocapacitance)**
- **Hybrid capacitors**
  - **Electrodes: special electrodes with significant double-layer capacitance and pseudocapacitance**

Supercaps vs. Batteries and Caps



Capacitors

- **fast charging** and discharging (≪ sec)
- high life time
- **high operating voltages**
- high power output
- **low energy capacity**

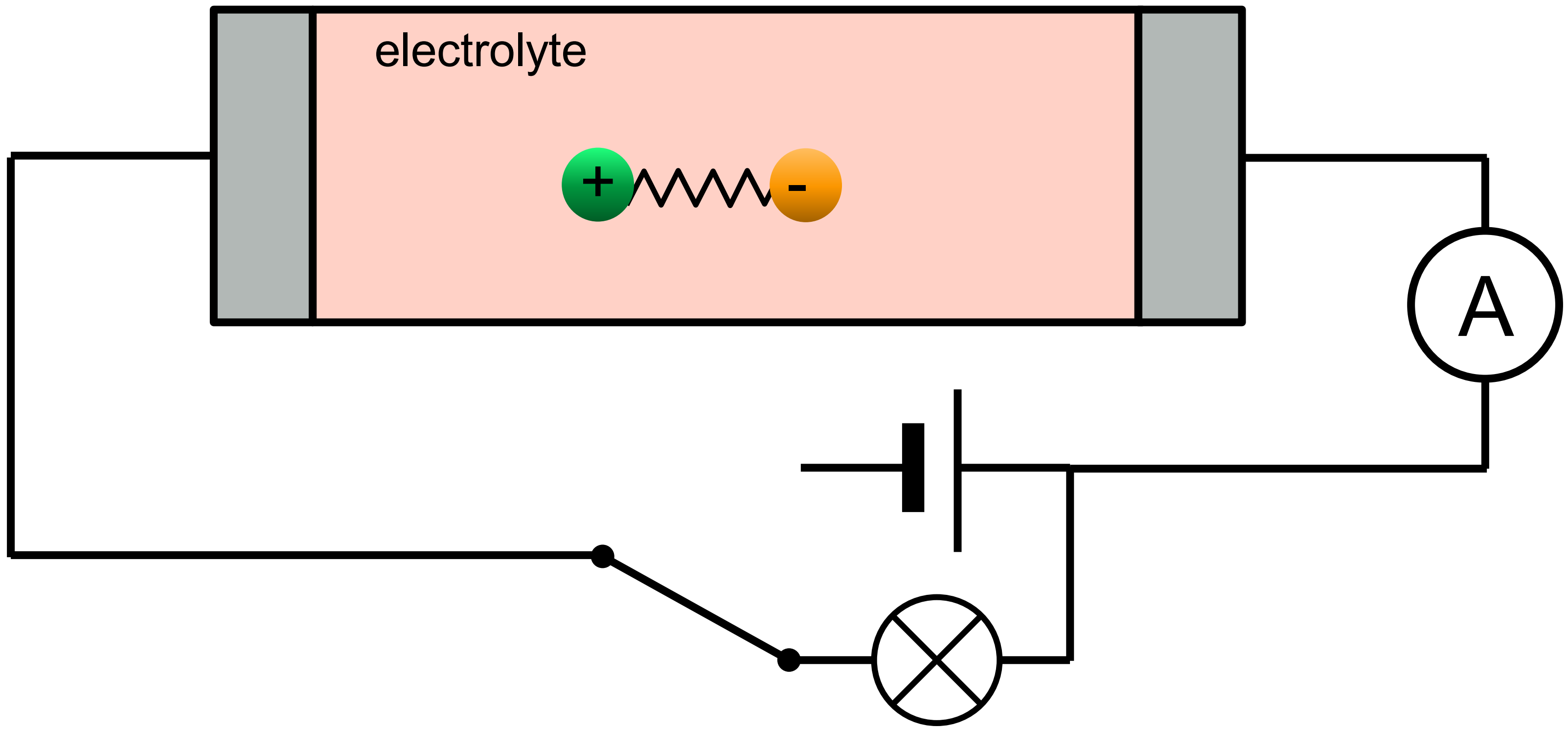
<u>Supercaps</u>

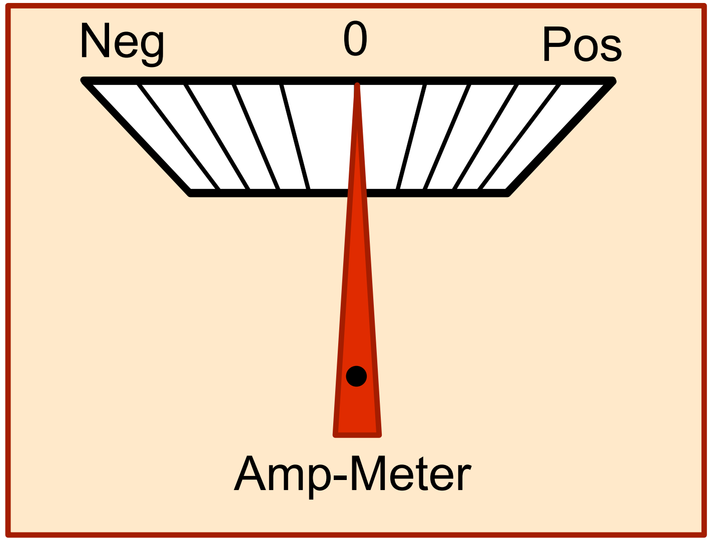
- **fast charging** and discharging (min – sec)
- high life cycle (≈ 500,000 cycles)
- **high power output**
  - **≈ 10 times higher than Li-ion battery**
- **low energy capacity**
  - **≈ 30 times lower than Li-ion battery**
- linear voltage dependence

Batteries

- **High energy capacity**
- Constant voltage dependence
- **low power output**
- low life expectancy (≈ 1000 cycles)
- **long charging** time (hours)

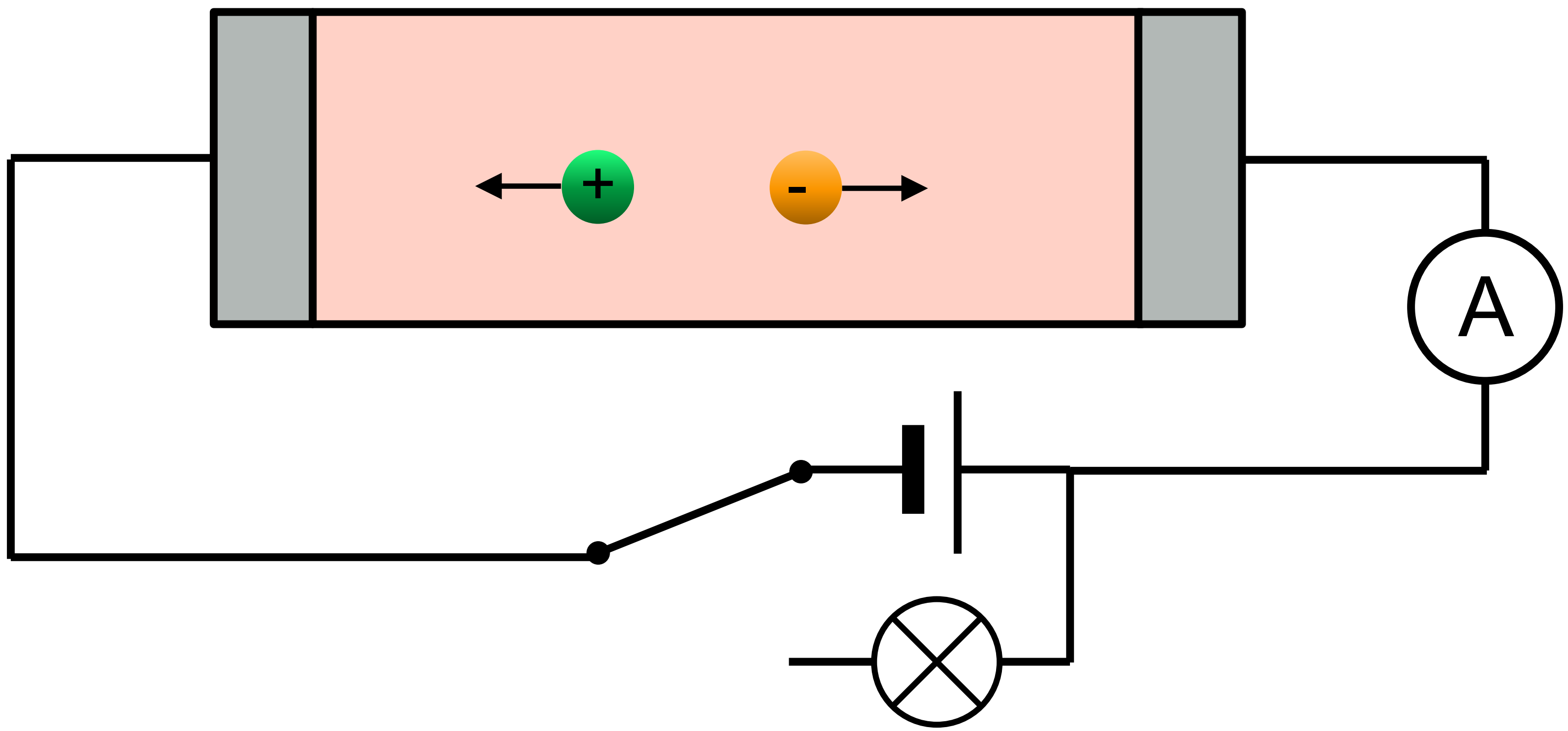
Energy Storage - Charge Separation

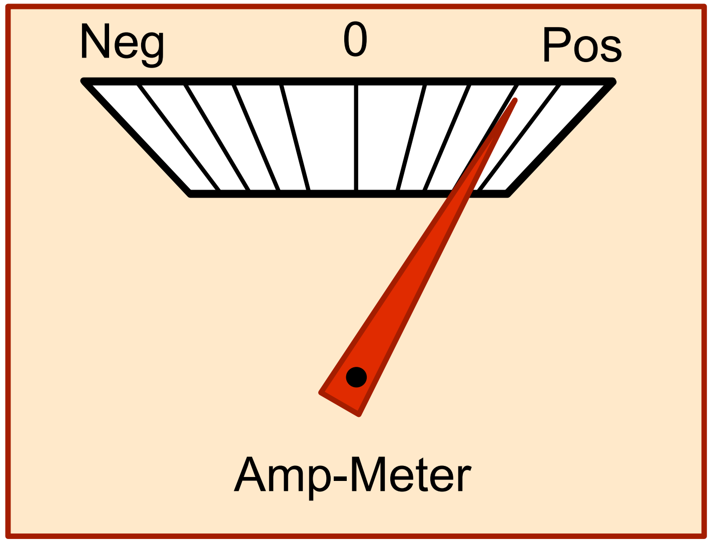




Discharged State:
1) no voltage is applied to electrodes
2) anions and cations are in close vicinity to each other
3) Movement of anions and cations governed by electrostatic interaction and diffusion processes

Energy Storage - Charge Separation

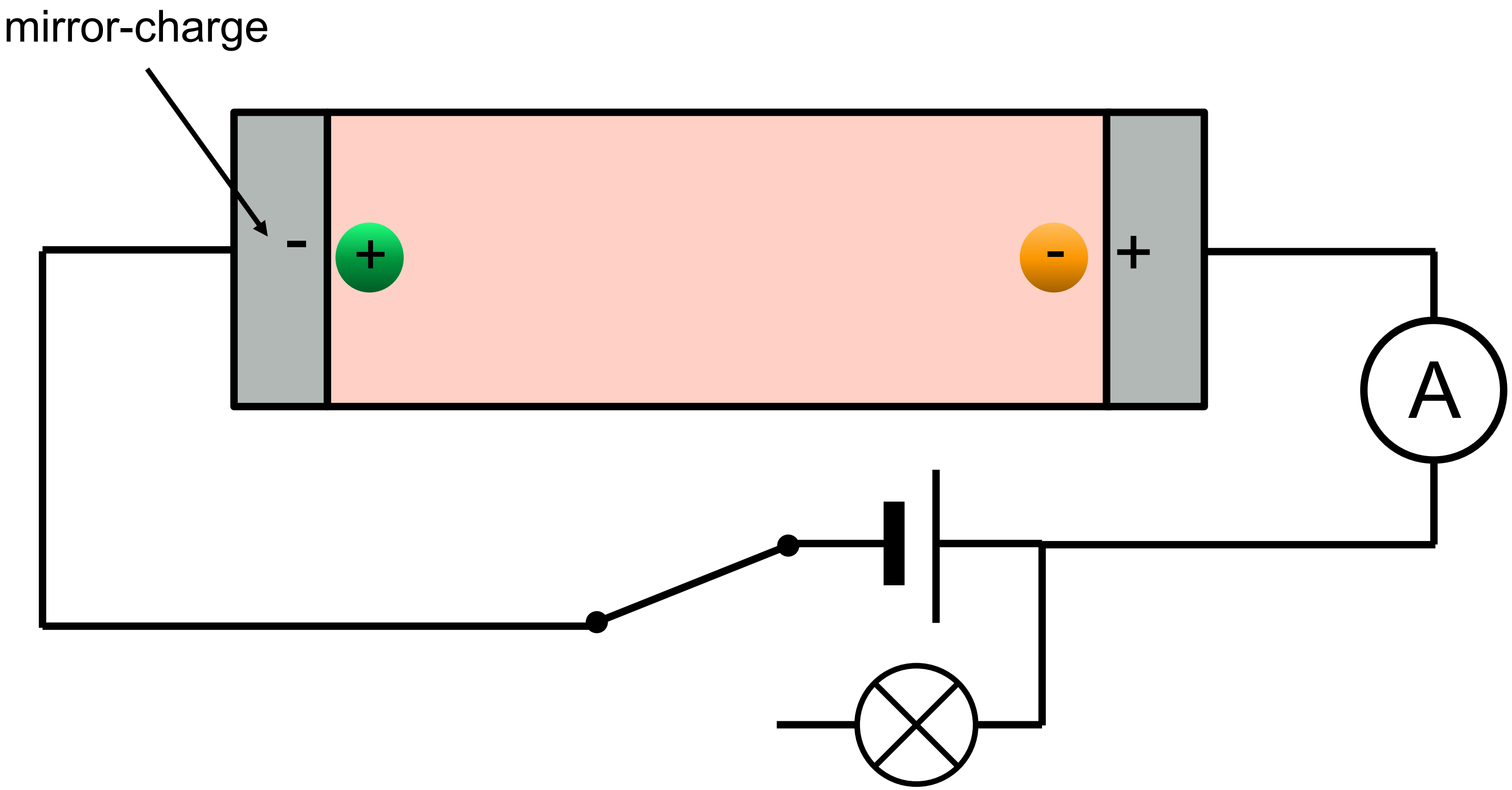


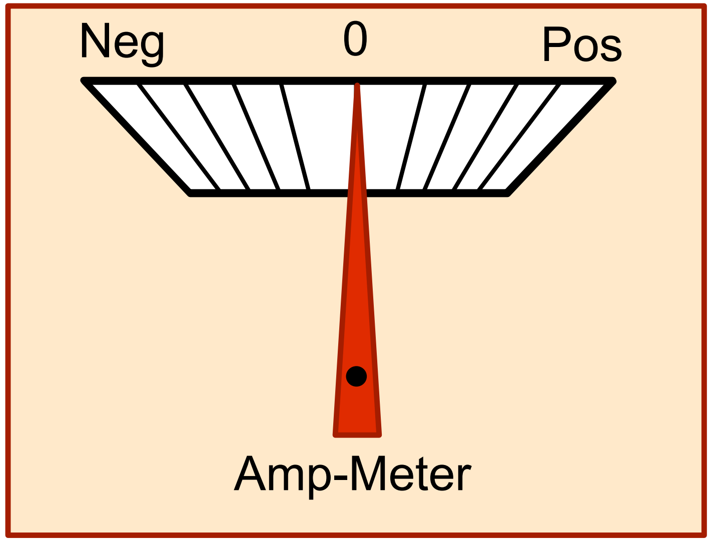


Charging:

1) voltage between plates (i.e. electric field) is applied
2) electric field “tears” charges apart
3) movement of the charges causes a current, provided by the voltage source

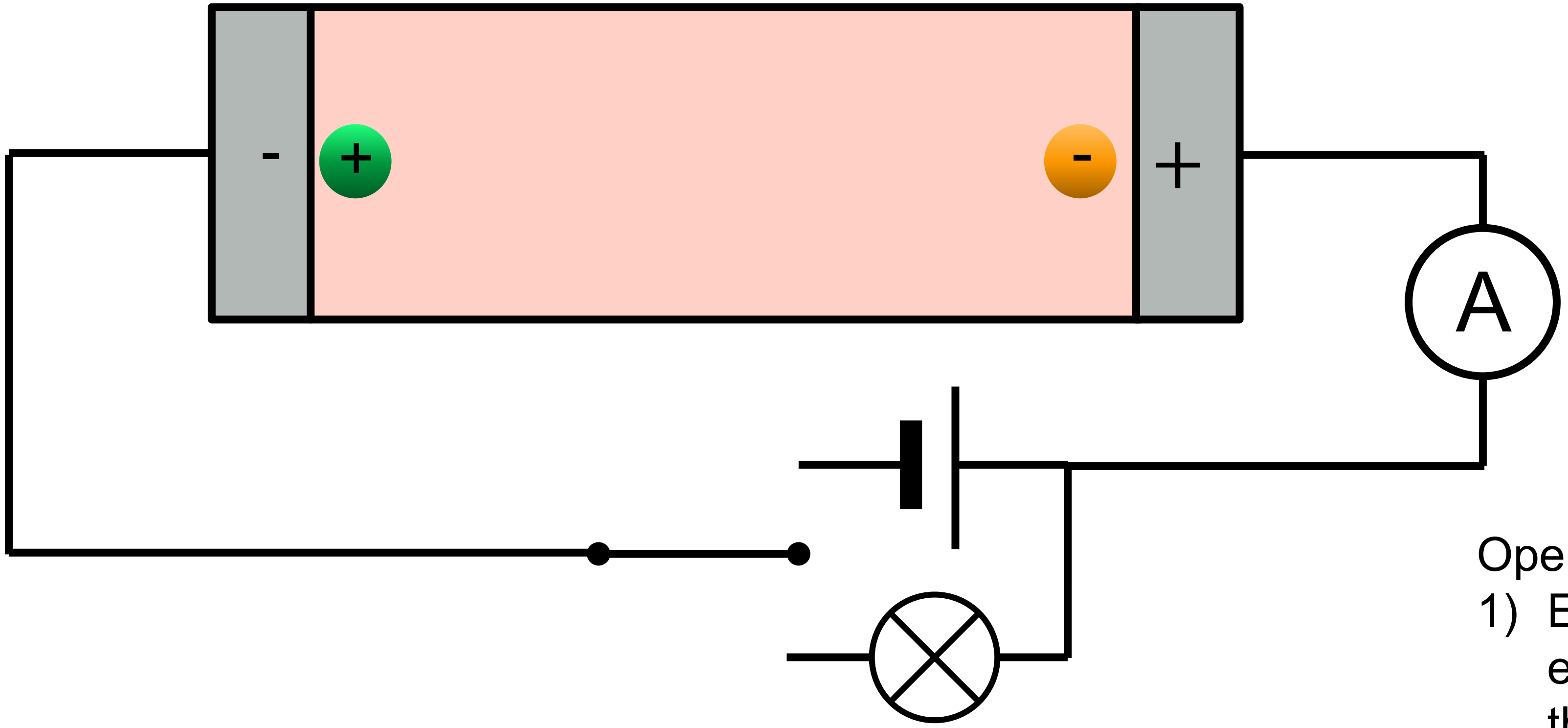
Energy Storage - Charge Separation

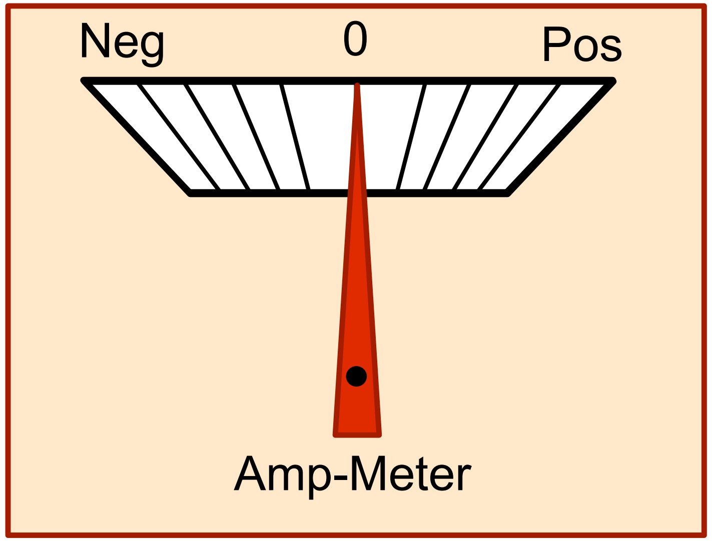




Fully charged:
1) anions and cations reach interface/electrode
2) Reorientation of charges comes to hold
3) Each anion/cation is mirrored by a opposing positive/negative charge at the electrode

Energy Storage - Charge Separation

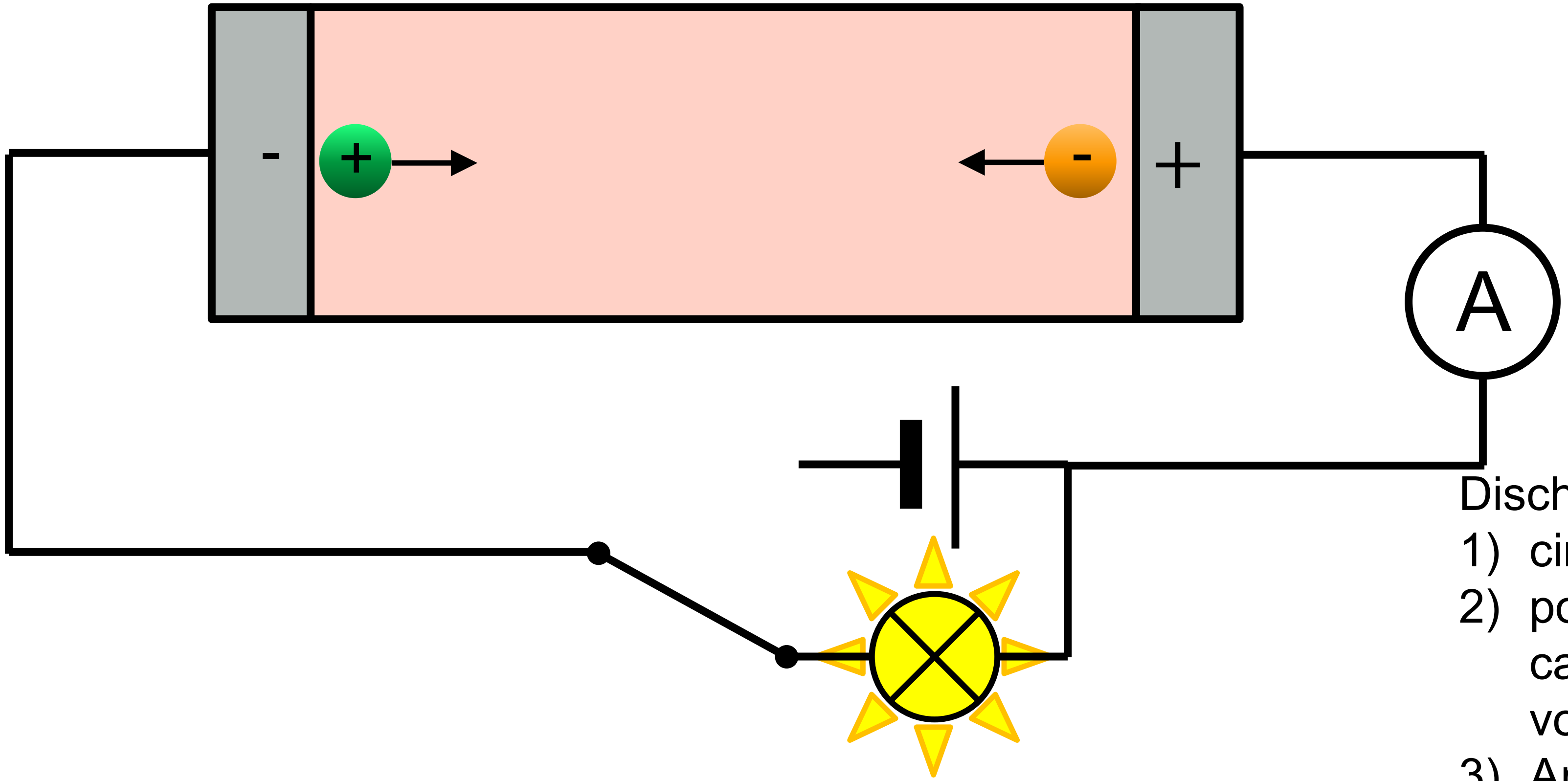


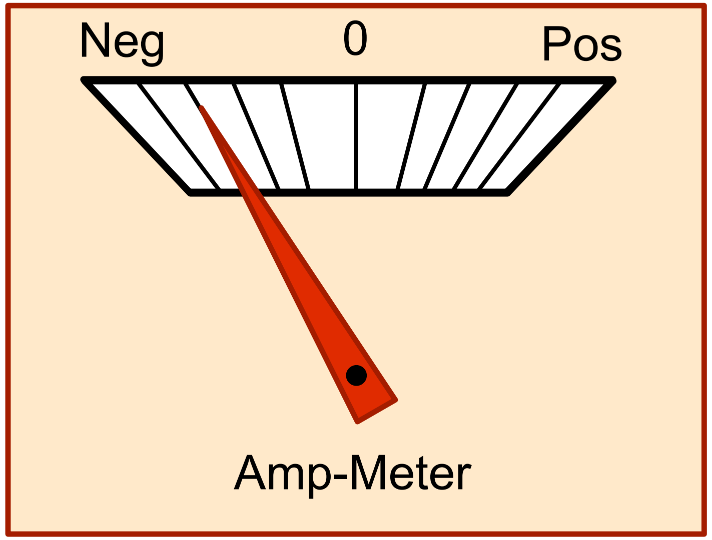


Open circuit:

1) Each anion/cation is balanced by an equal amount of mirror charge at the interface
2) Anions and cations reside a the interface
3) Charges can be stored at interface for a long time

Energy Storage - Charge Separation

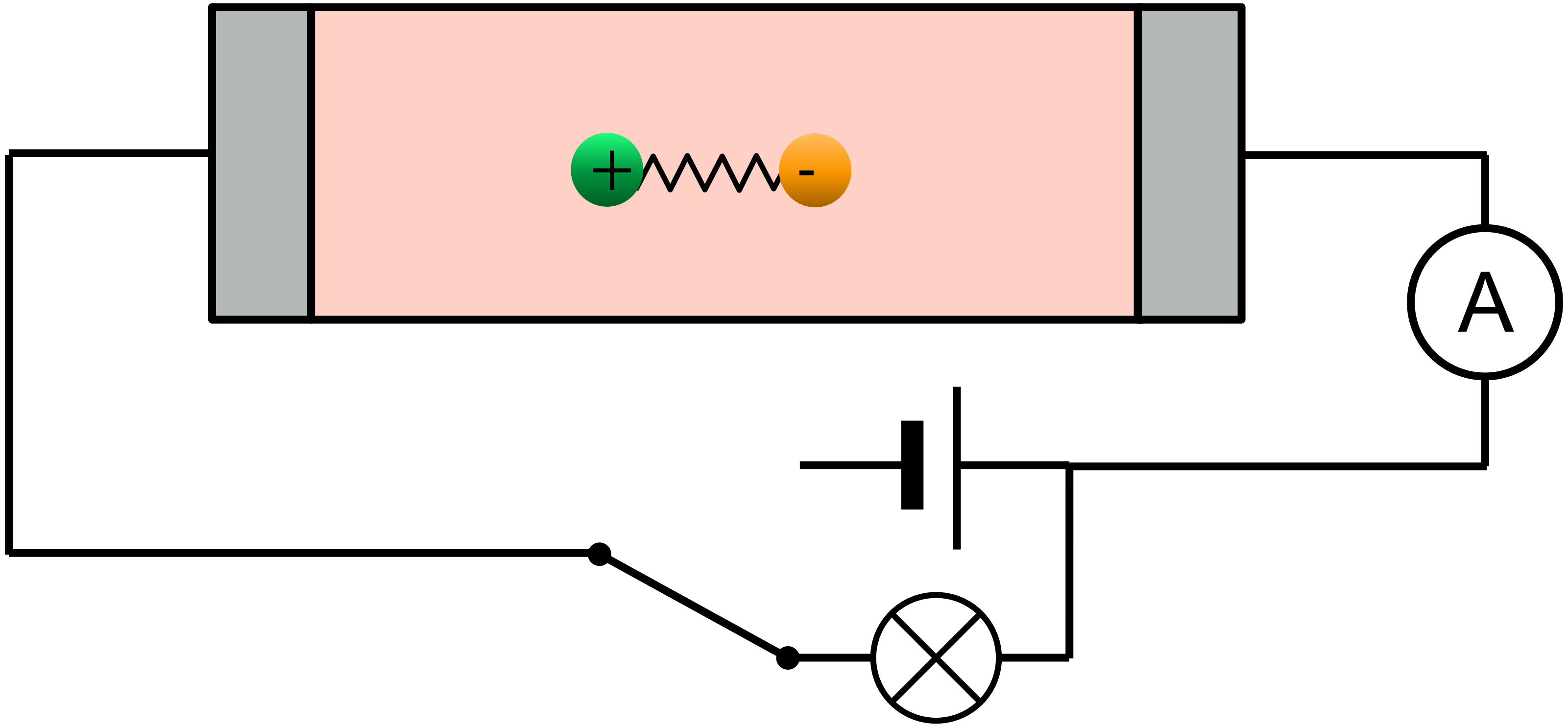


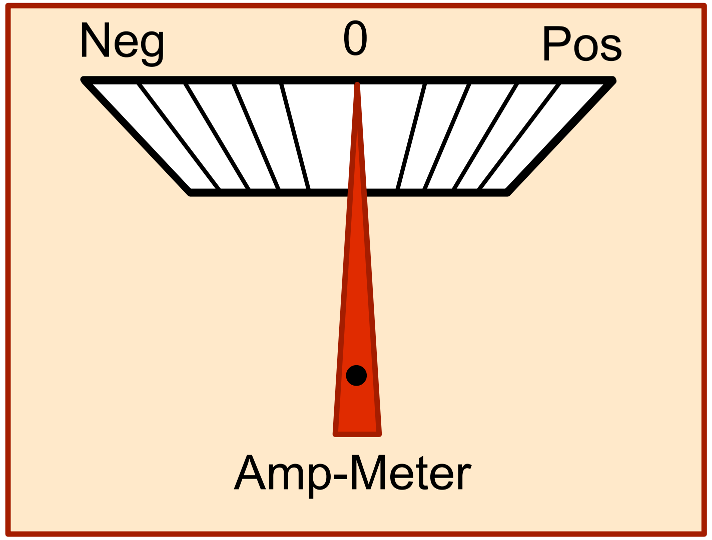


Discharge process:

1) circuit is closed
2) potential difference between the plates, causes electrical current at a certain voltage
3) Anion/cations “loose” their mirror charge, leading to charge movement
4) The quicker the anions/cations can be released, the larger the current

Energy Storage - Charge Separation





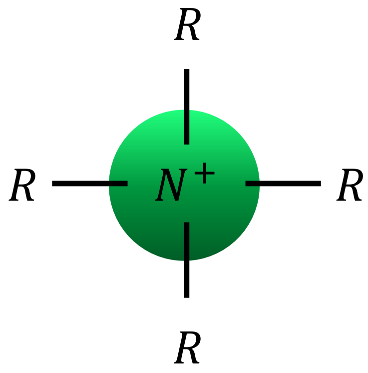
Discharged State:

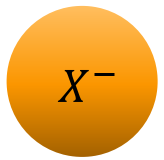
1) no voltage is applied to electrodes
2) anions and cations are again in close vicinity to each other
3) movement of anions and cations governed by electrostatic interaction and diffusion processes

Structure of EDLC

Electrolytic System:

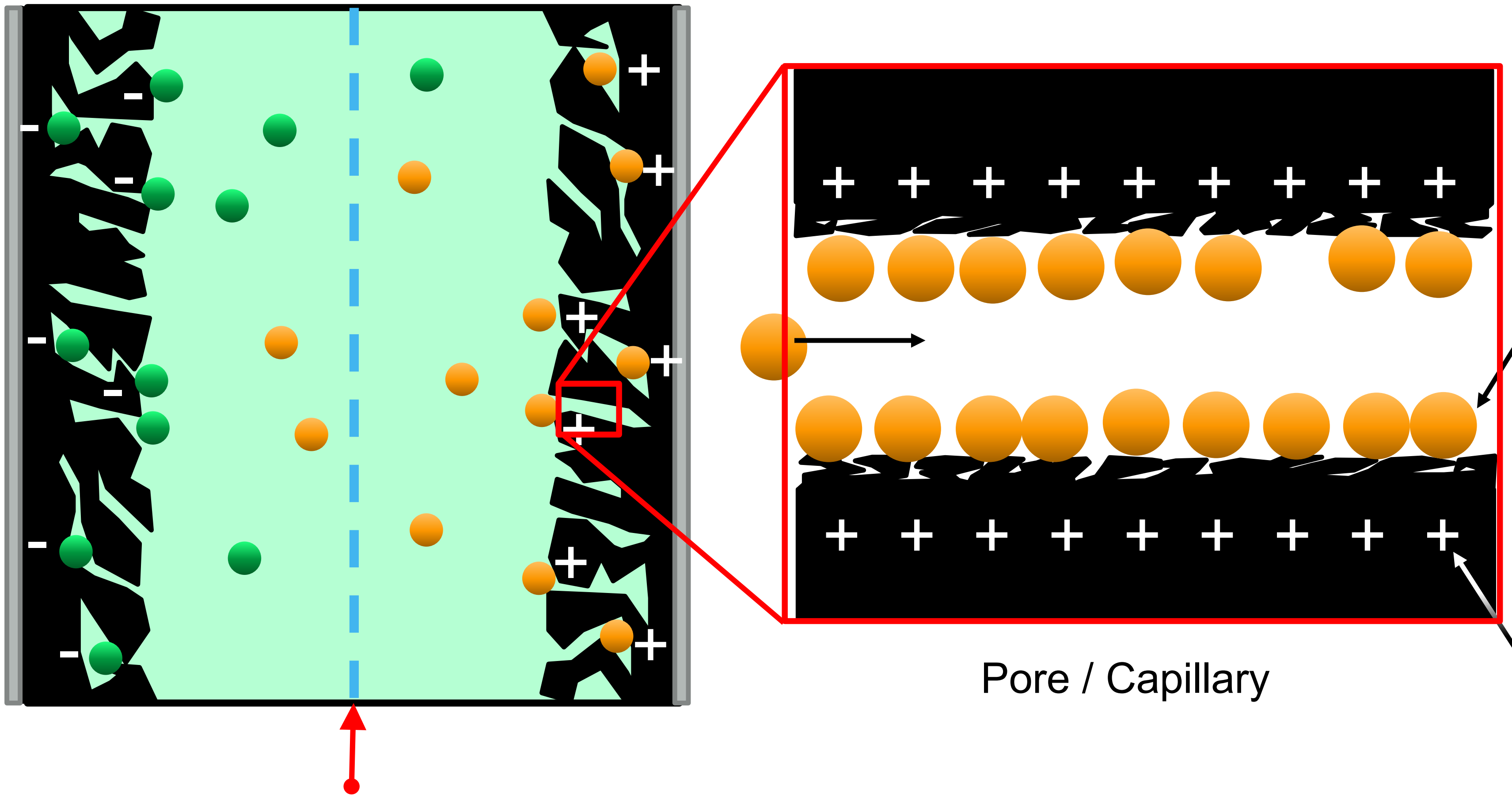
- Ammonium salt with counter ion





- Acetonitrile

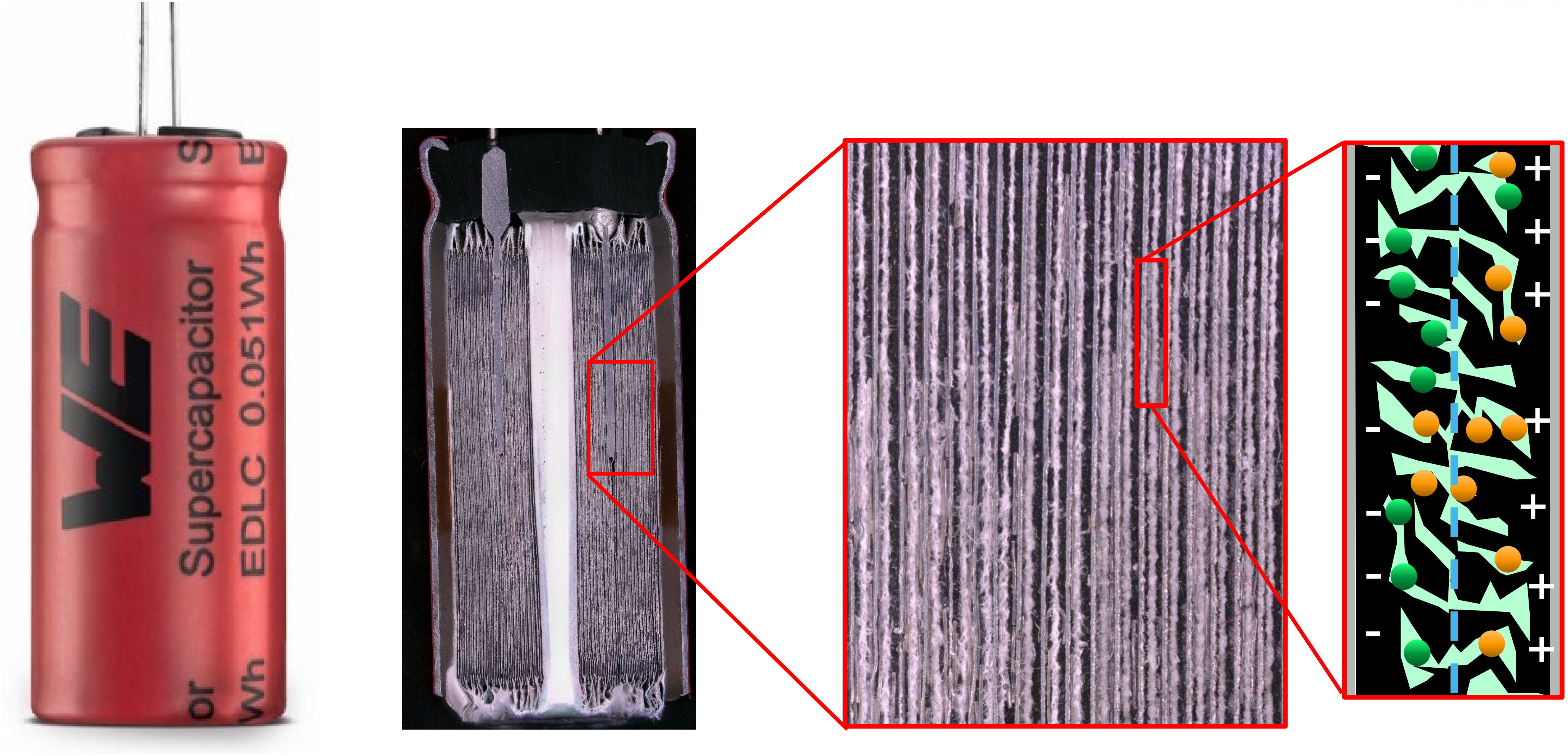
$$H_3C-C\equiv N$$



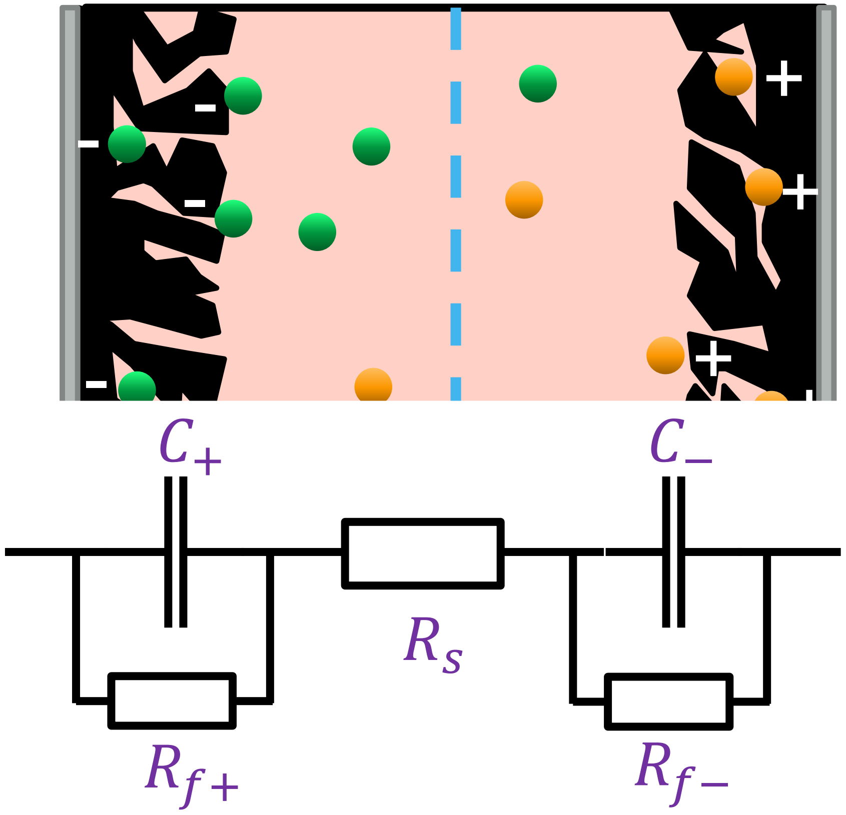
Helmholtz (double) layer:

- Ionic charge is balanced by mirror-charge

Structure of EDLCs



Physical Processes and Parameters

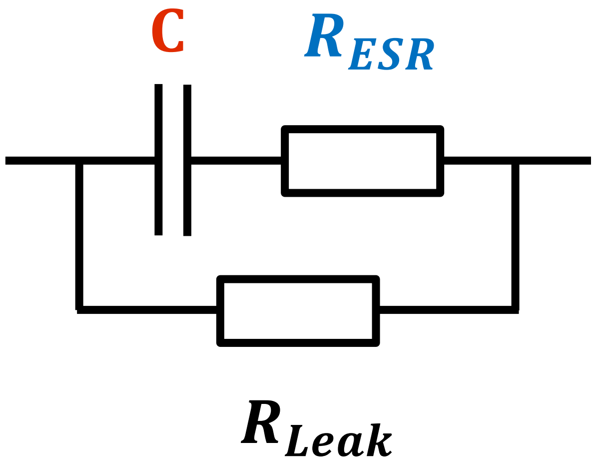


equivalent circuit

$$\frac{1}{C_+} + \frac{1}{C_-} = \frac{1}{\mathbf{C}}$$

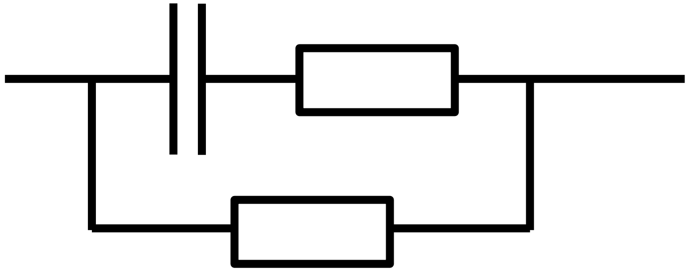
$$R_s \sim \boldsymbol{R_{ESR}}$$

$$R_s + R_{f+} + R_{f-} \sim \boldsymbol{R_{Leak}}$$



equivalent circuit

Parameter and Performance



Basic Parameters:

- U_r, **Rated Voltage:**
  - is not determined by the equivalent circuit but by electrochemistry (Decomposition Voltage)
    - Non-Aqueous Electrolyte (typ.): $\approx 2\,V$ ... $3V$
    - Aqueous Electrolyte (typ.): $\approx 1.5\,V$
- C, **Capacitance:**
- R_{ESR}, **ESR:**
- R_{Leak}, **Leakage:**
  - Influence on charge storing capabilities ($R_{Leak} \approx 10\ \text{k}\Omega \ldots 1\ \text{M}\Omega$)

Performance Parameters:

- **Energy storage capacity:**

$$E = \frac{1}{2} \times C \times U_r^2$$

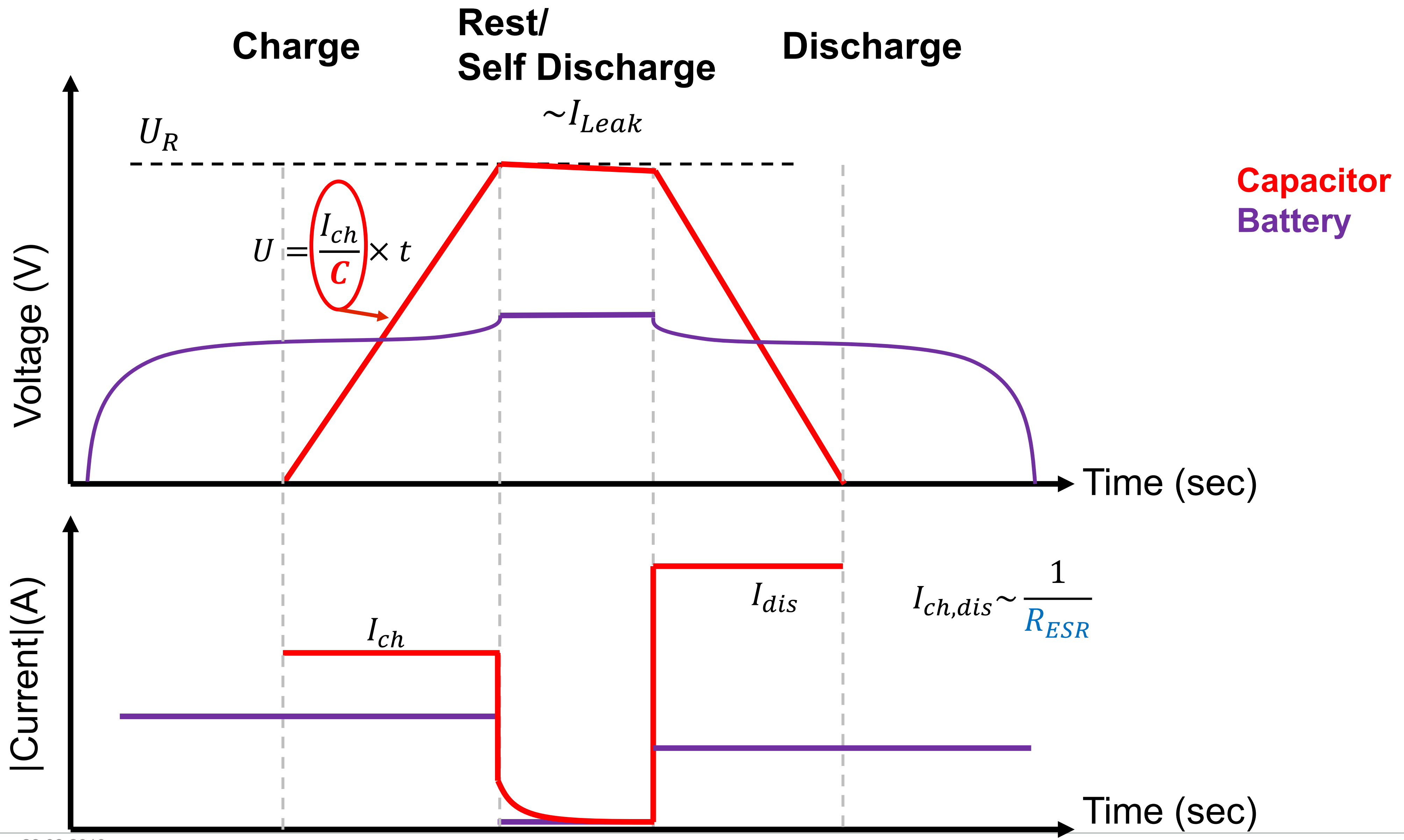
- **Maximum Power output:**

$$P_{max} = \frac{U_r^2}{4\,R_{ESR}}$$

- ***Characteristic R-C Time:***

$$\tau = R_{ESR} \times C$$

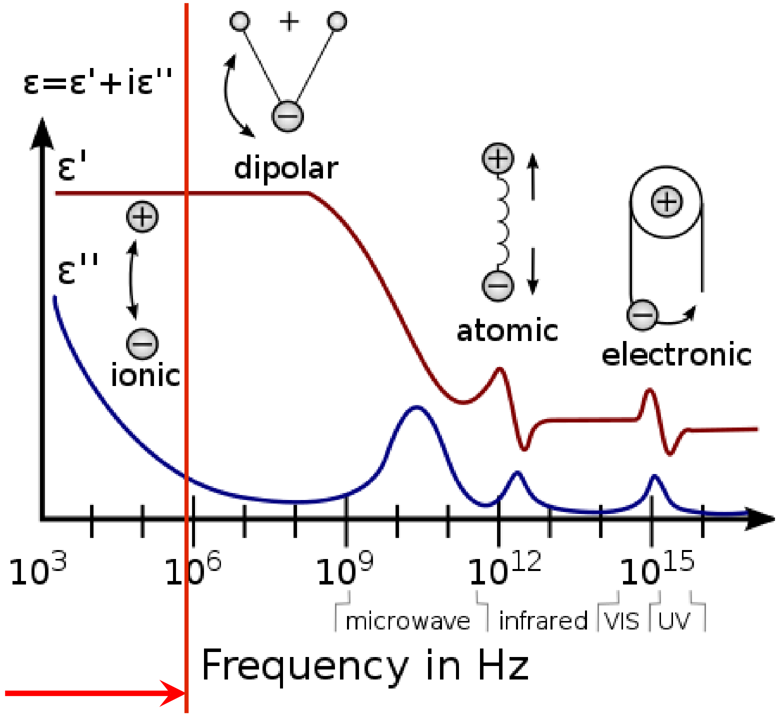
Charge and Discharge Behavior



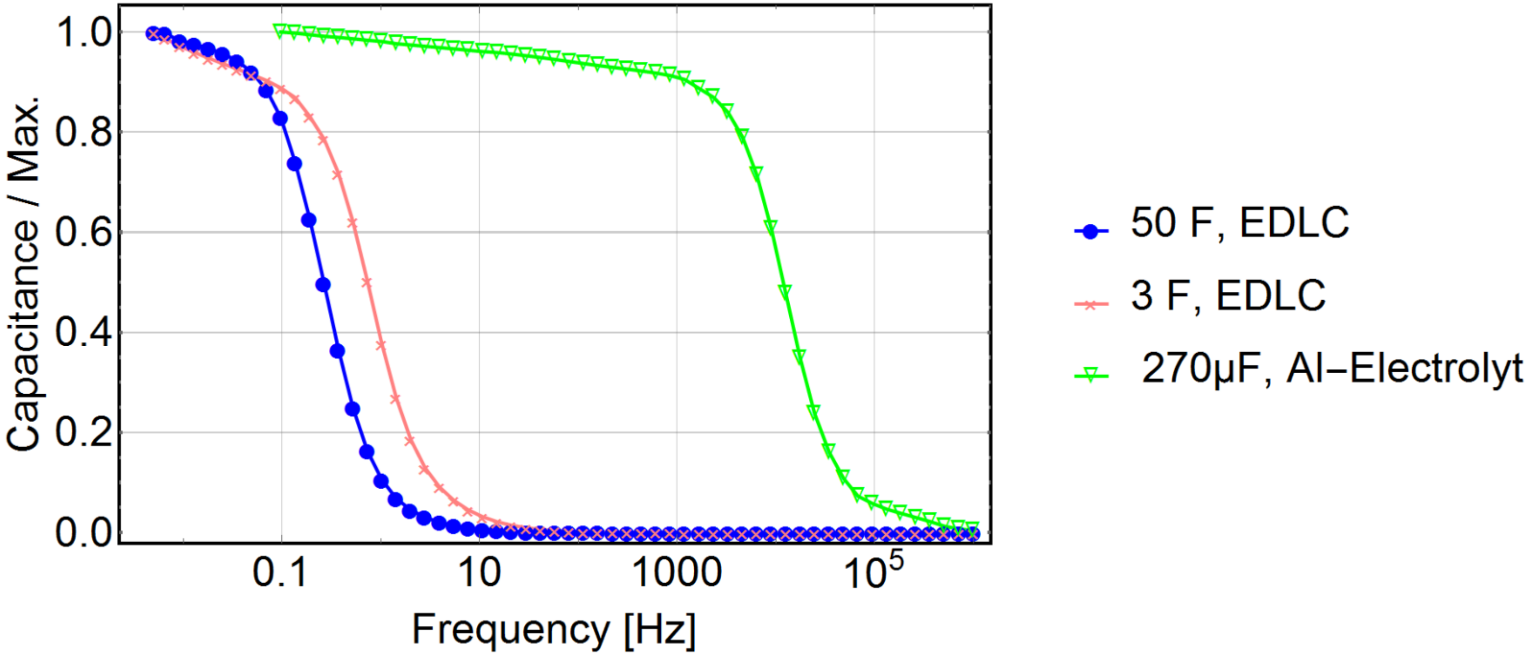
Impedance Spectra

Dielectric (impedance) spectroscopy:

- "measures" polarizability of a medium as a function of frequency



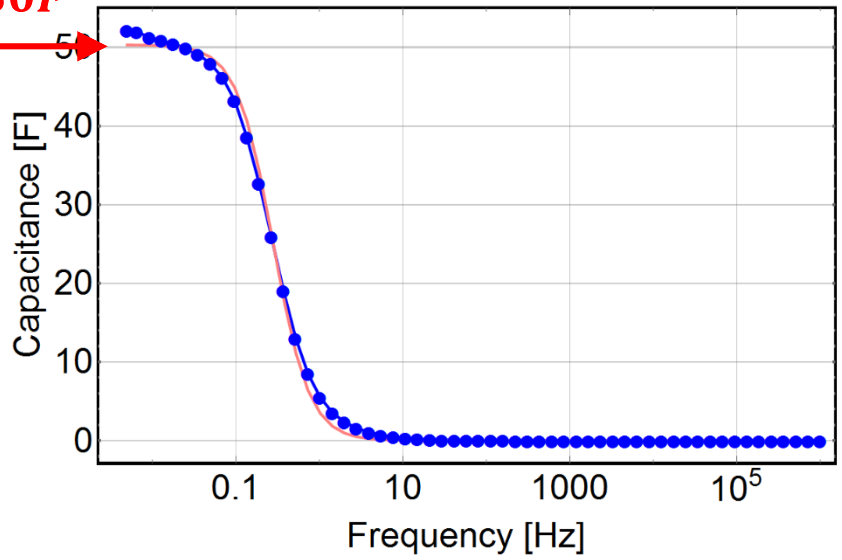
Range of interest: 1 mHz … 1 MHz

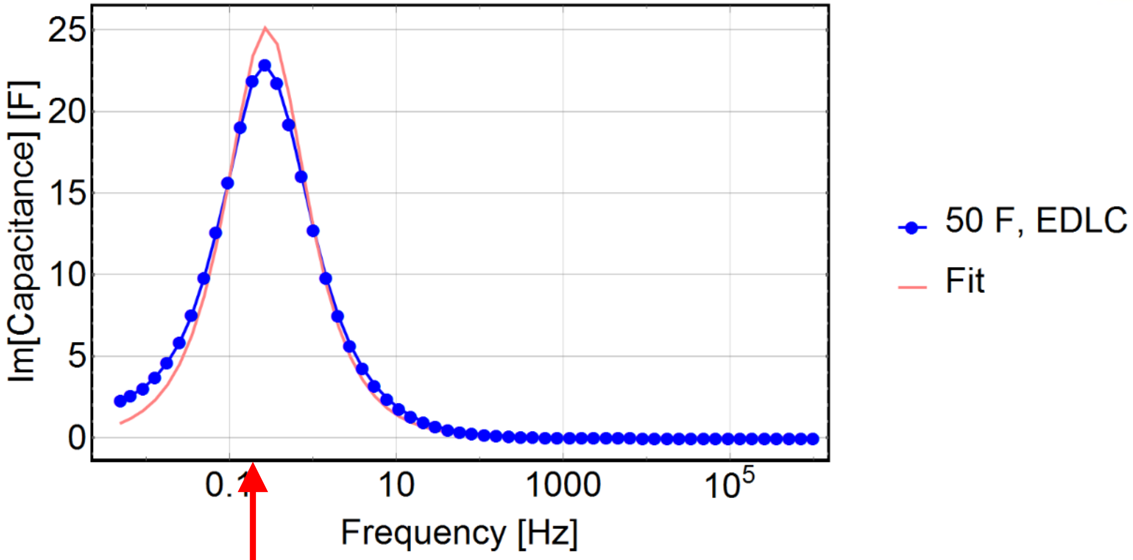


Source: *Wikipedia: "https://en.wikipedia.org/wiki/Dielectric_spectroscopy"*

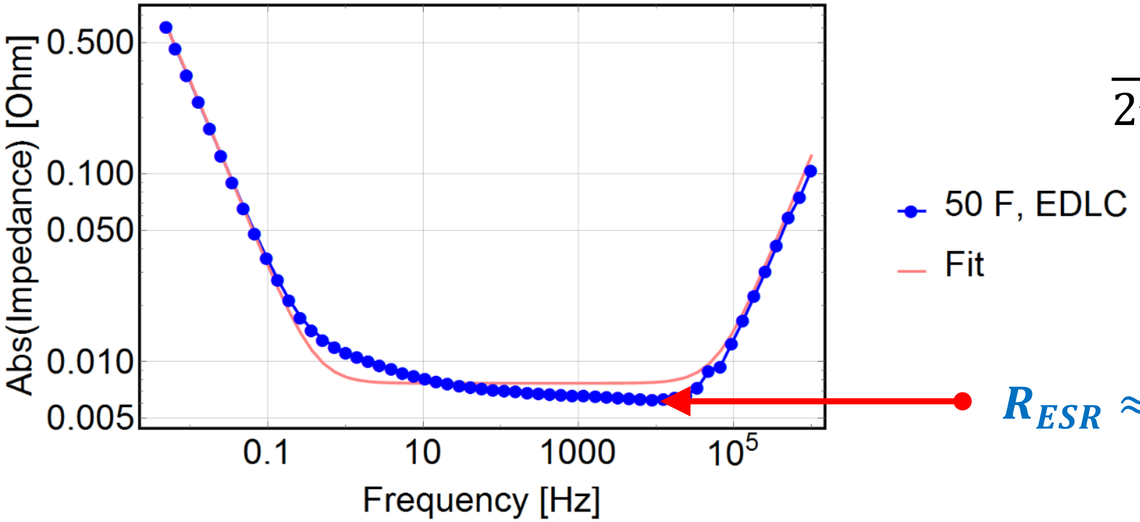
Impedance Spectra

$C \approx 50F$





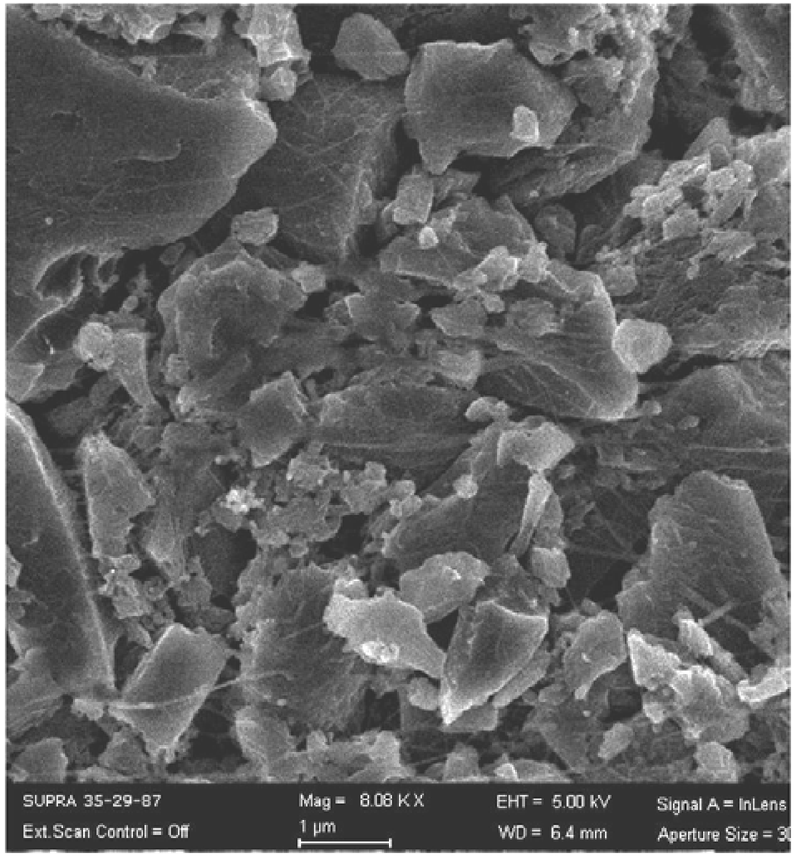
$$\frac{1}{2\pi\, R_{ESR} C} \approx 0.29Hz$$



$R_{ESR} \approx 7\ \text{m}\Omega$

Fit results:
$R_{ESR} = 0.011\ \Omega$,
$\mathbf{C} = 50.3\ \text{F}$

Physical Limitations of Capacitance



$$\frac{C}{m} \sim \frac{A}{m}$$

C: capacitance
m: mass of a.c.
A: specific area of a.c.

Specific surface area of a. c.:
$$A^* = \frac{A}{m} \quad \left[\frac{\mathrm{m}^2}{\mathrm{g}}\right]$$

Specific capacitance of a. c.:
$$C^* = \frac{C}{m} \quad \left[\frac{\mathrm{F}}{\mathrm{g}}\right]$$

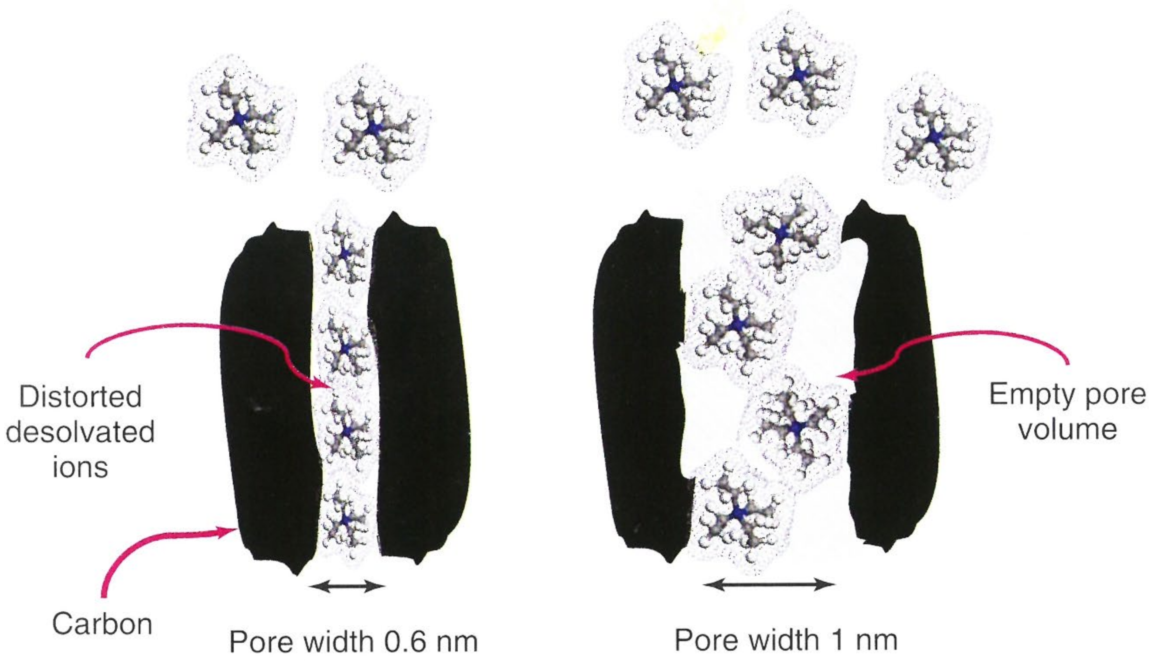
Example of calulation: 50F EDLC contains ≈ 2.2 g a. c.

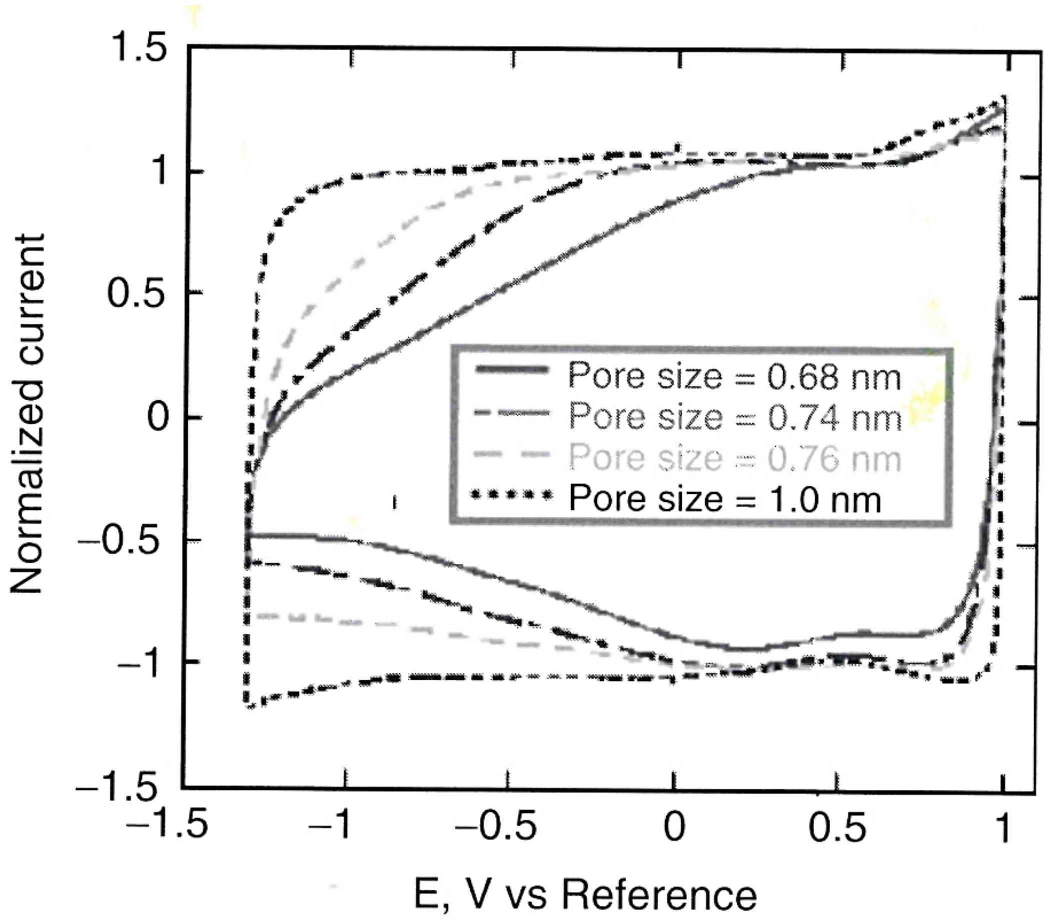
	m [g]	$A^* \left[\frac{\mathrm{m}^2}{\mathrm{g}}\right]$	A [m^2]	$C^* \left[\frac{\mathrm{F}}{\mathrm{g}}\right]$	C [F]
Comm.		500	**1120**	24	**54**
Micro.	2.2	935	**2095**	142	**318**
Micro.		2312	**5179**	113	**253**

Source: **Activated carbon based electrodes in commercial supercapacitors and their performance**, *V. Obreja et al., International Review of Electrical Engineering (2010)*

Physical Limitations of Capacitance

Pore Accessibility:





Source: ***Supercapacitors Materials, Systems and Applications***, *ed. F. Beguin et al., WILEY-VCH (2013)*

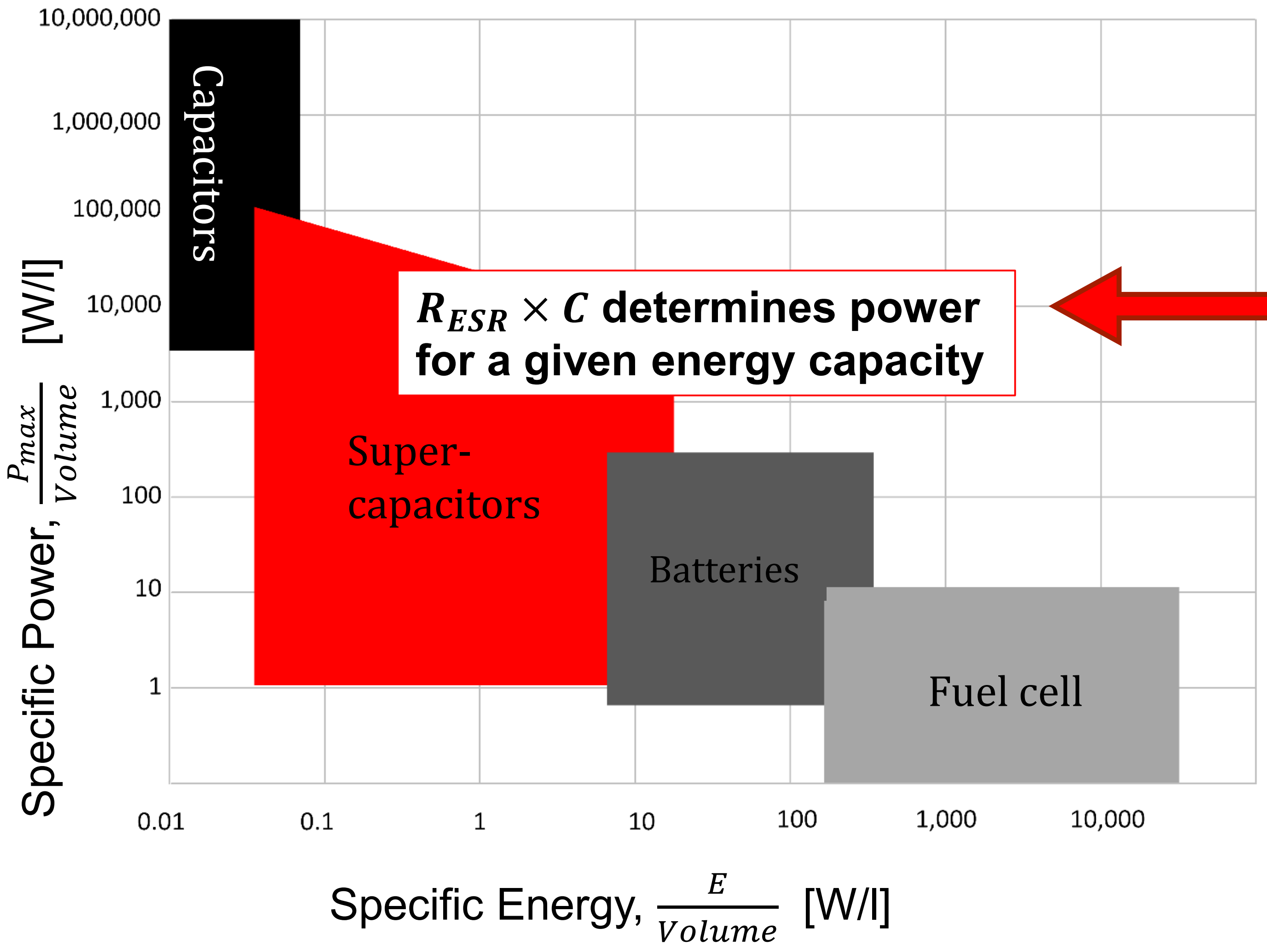
Parameters – Device Properties

$\tau = R_{ESR} \times C$	$\leftrightarrow$	• fast charging and discharging (min – sec)
low R_{ESR}	$\leftrightarrow$	• high power output • ≈ 10 times higher than Li-ion battery
charges are only stored at the interface	$\leftrightarrow$	• low energy capacity • $\approx$ 30 times lower than Li-ion battery
ELDC are capacitors	$\leftrightarrow$	• linear voltage dependence
U_r < Decomposition Voltage	$\leftrightarrow$	• low operating voltage

Thank you for your attention.

Additional Slides / Take Outs.

Parameter and Performance



$R_{ESR} \times C$ determines power for a given energy capacity

$$P(E) = \frac{2}{R_{ESR} \times C} E$$

C and U_r determine the energy capacity

$$E = \frac{1}{2} \times C \times U_r^2 \ ,$$

Impedance Spectra

- electrical model is equal to that for MLCC, ELKOs, …
- inductive reactance (neglectable)

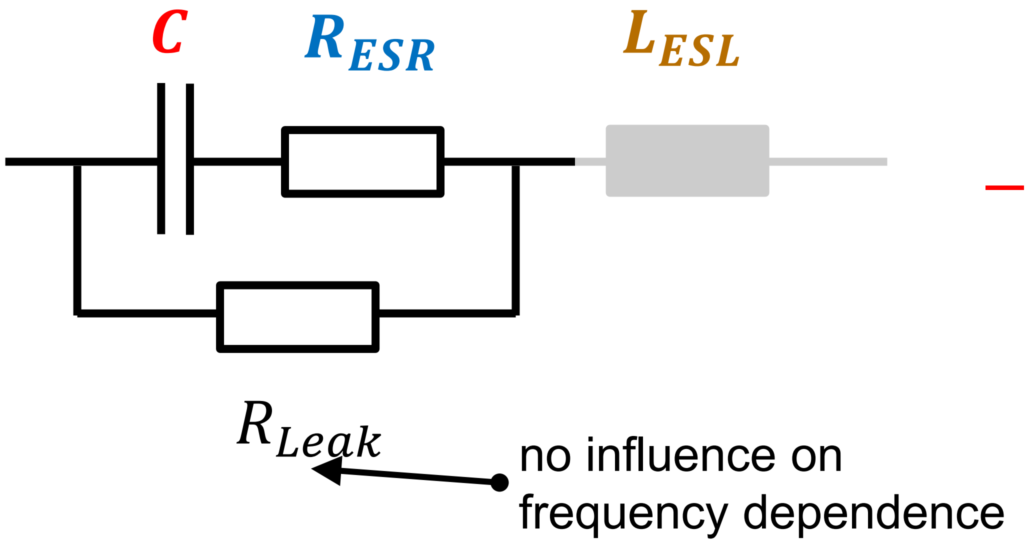
$X_L = \omega \times L_{ESL}$

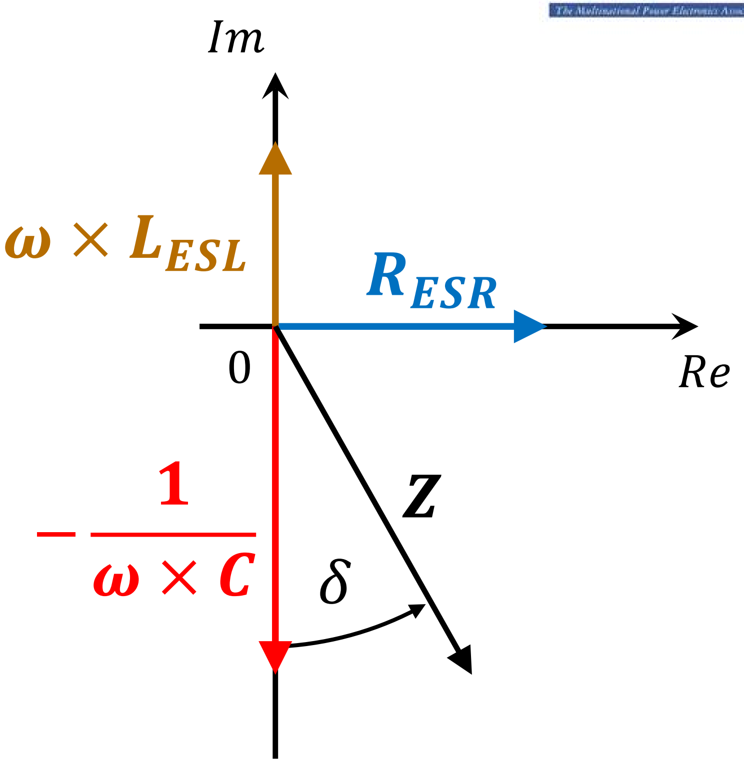
- capacitive reactance

$X_C = -\frac{1}{\omega \times C}$

- impedance

$\hat{Z} = R_{ESR} + jX_L + jX_C$





$DF = \tan(\delta)$

$\hat{Z} = \frac{1}{j\omega\hat{C}}$ $\quad \hat{C} = \frac{C}{1 + (\omega\, R_{ESR}\, C)^2} - j\frac{\omega C^2 R_{ESR}}{1 + (\omega R_{ESR}\, C)^2}$

$\omega = 2\pi f, \quad \sqrt{-1} = j$