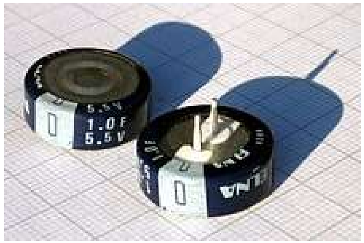
(Super) Capacitors



Faster (dis)charging

Batteries are a good charge-storage solution, but are limited in how quickly they can discharge (safely).

- Ultimately, redox processes can only occur so fast...

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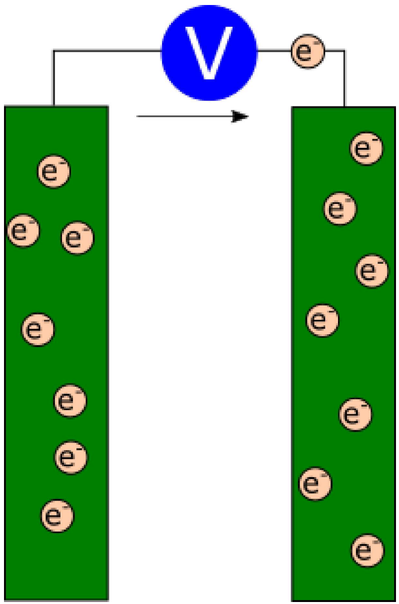
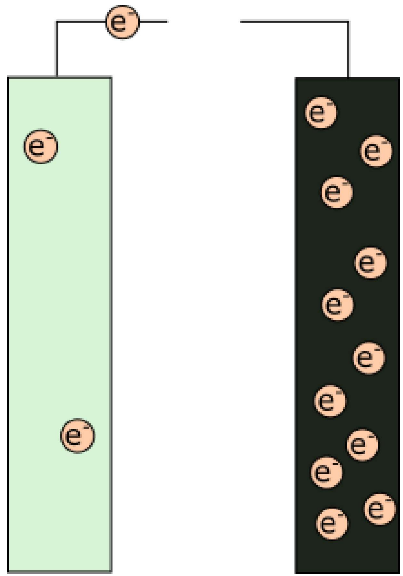
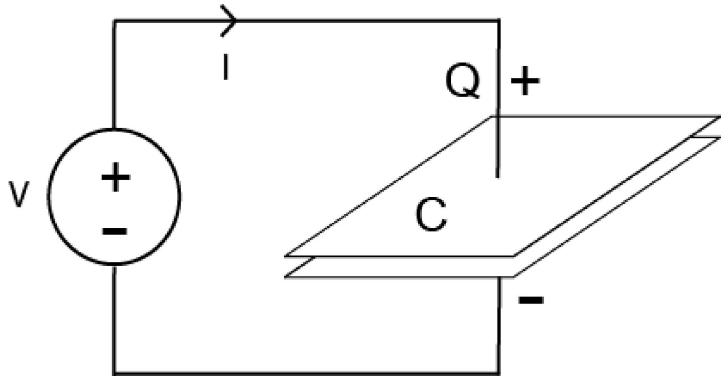
Why not separate charges directly?





This is a **Capacitor**

An arrangement of electrodes of area *A*, separated by a distance *d*.



Two electrodes separated by vacuum have a capacitance *C*:

$$C = \frac{\epsilon_0 A}{d}$$

where ε_0 is the permittivity of free space = 8.854×10^{-12} C^2 J^{-1} m^{-1}

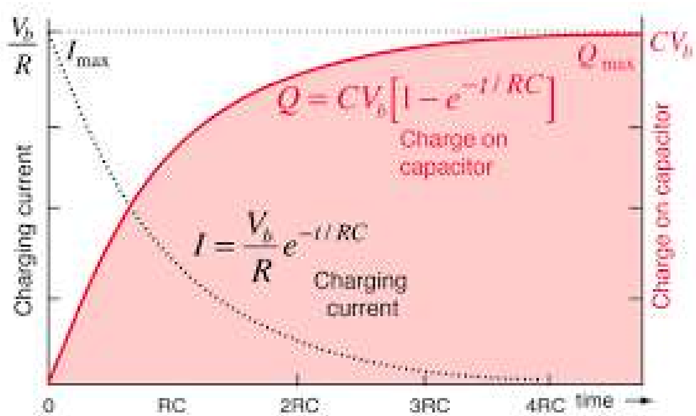
Charge stored

On charging a capacitor with a constant voltage, current decays with time:

$$I_t = I_0 e^{\left(\frac{-t}{RC}\right)}$$

The charge stored increases with time:

$$Q_t = CV\left[1 - e^{\left(\frac{-t}{RC}\right)}\right]$$



The maximum charge stored, $Q = CV$

Increasing the charge stored

$C = \frac{\epsilon_0 A}{d}$, so decreasing d or increasing A will increase stored charge. If d gets too small, however, electrons will tunnel from one plate to the other.

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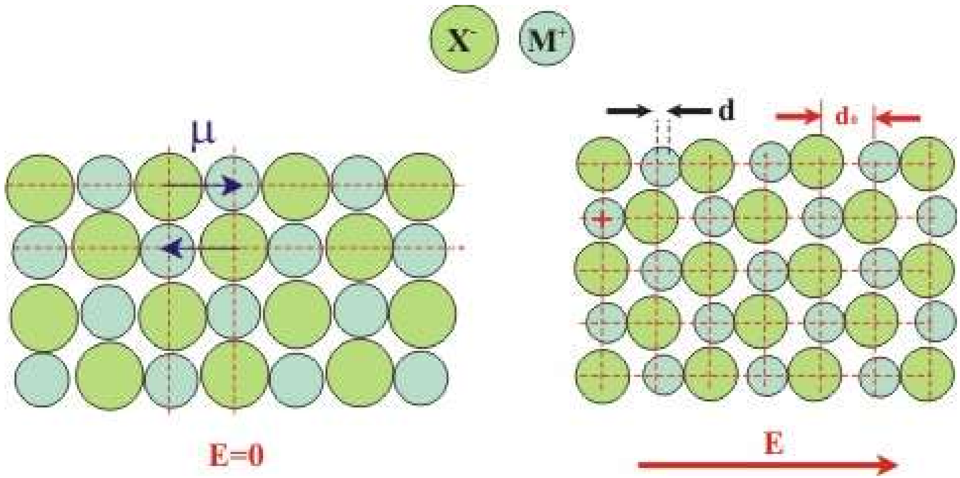
Alternatively, use a **dielectric**

- *An electrically insulating material in which an applied electric field causes a **displacement** (but not a flow) of charge.*

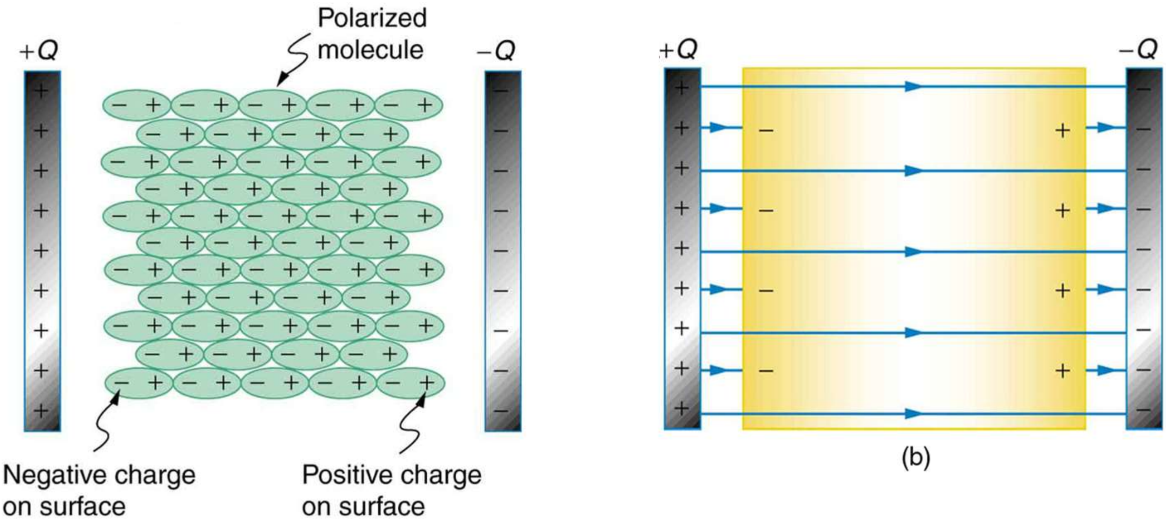


Dielectric capacitor

Adding a dielectric between the plates increases the charge capacity.

$$C_{\text{dielec}} = \frac{\epsilon_r \epsilon_0 A}{d}$$

where ε_r is the relative permittivity of the dielectric ($\varepsilon_r = \varepsilon / \varepsilon_0$) and $\varepsilon_r > \varepsilon_0$



(a) (b)

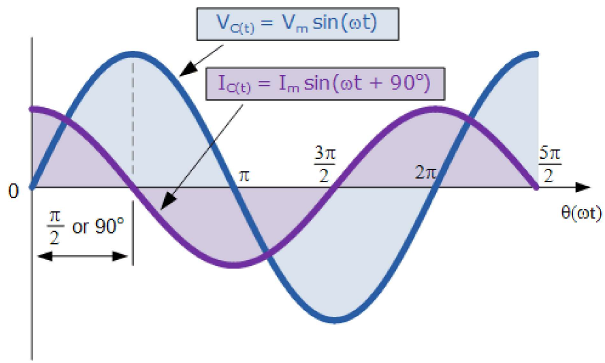
Example permittivities

Material	Relative Permittivity, ε_r
Vacuum	1
Paper	2.0 - 6.0
Polymers	2.0 - 6.0
Silicon oil	2.7 - 2.8
Quartz	3.8 - 4.4
Glass	4 - 15
Al_2O_3	10
Ta_2O_5	26
TiO_2	100
$CaTiO_3$	130
$SrTiO_3$	285
$BaTiO_3$	1000 - 10000

Characterising dielectrics

Apply an alternating (sinusoidal) field, and measure the resulting current *and phase shift* - **Impedance spectroscopy**

- Applied field, $E_t = E_0 \sin(\omega t)$, where $\omega = 2\pi f$
- Response current, $I_t = I_0 \sin(\omega t + \phi)$



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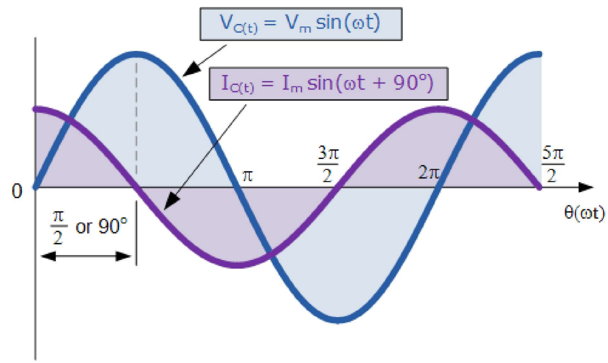


The total impedance $\left(Z(\omega) = \frac{E_t}{I_t}\right)$ can be represented as a complex number:

- $Z(\omega) = Z_0(\cos\phi + i\sin\phi)$

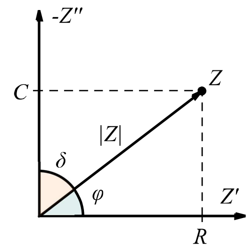
- In an ideal dielectric, current and voltage should be 90° out-of-phase (φ = 90°).
- For a resistive material, current and voltage should be in phase (φ = 0°).

https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/

Impedance analysis

Two standard ways to display data:

- **Nyquist plot**: -Z'' (90° out-of-phase) against Z' (in phase).
- **Bode plot**: |Z| and φ plotted against frequency



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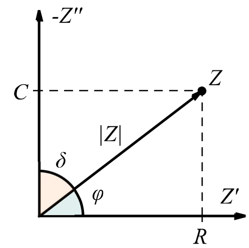
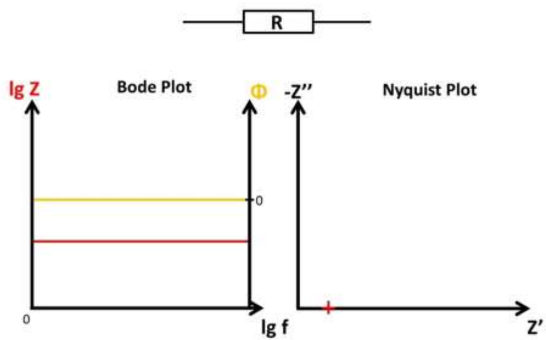
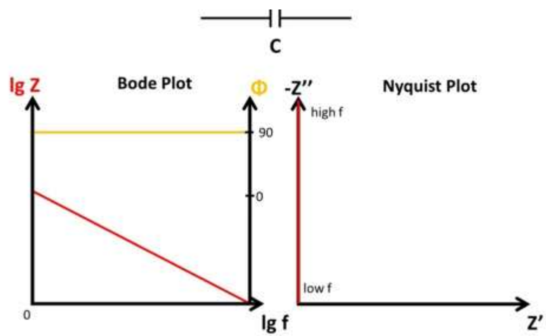


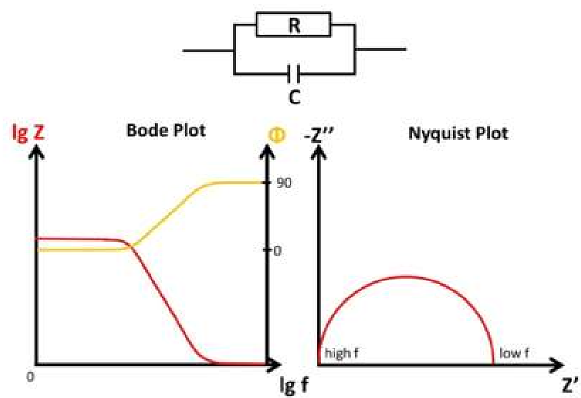
Ideal Response





'Real' Impedance

Many real materials exhibit behaviour like a parallel RC circuit:



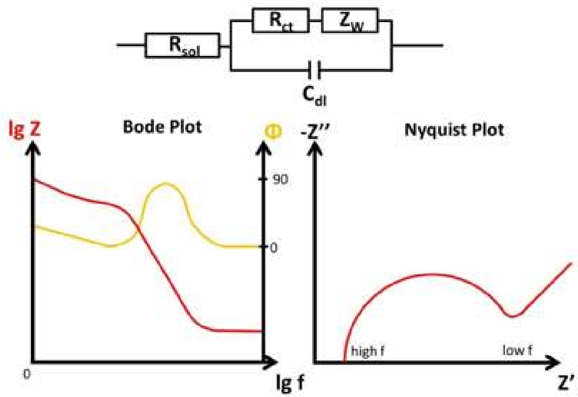
e.g.

- Ions flowing through a solution and building up a layer on the electrode (see later)
- Ionic conduction in a ceramic material building up a charge gradient

More complex behaviour is often observed, and can be modelled using *equivalent circuits*

Real dielectric response

Changing the electric field direction causes the dipoles to rearrange with a characteristic timescale. This timescale means *real* dielectrics show a peak in φ with frequency, corresponding to the maximum energy loss.



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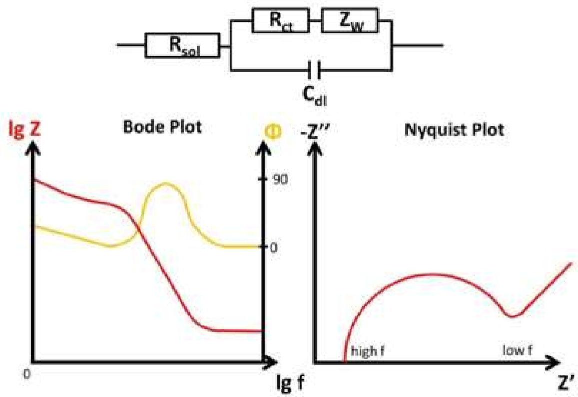
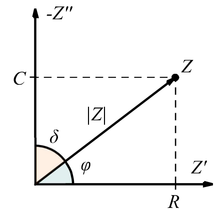


This *dielectric loss* is often characterised as $\tan\delta = \frac{Z'}{-Z''}$, where $\delta = 90^\circ - \phi$

- tan δ must be minimised for applications

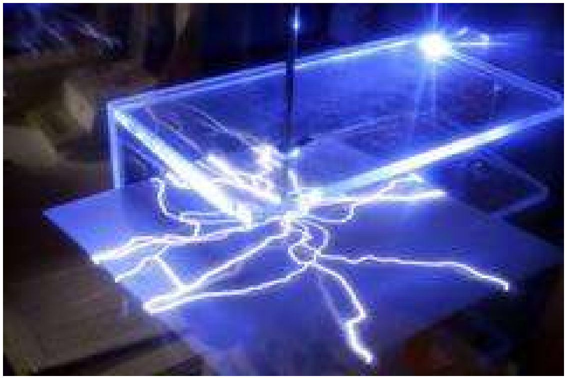


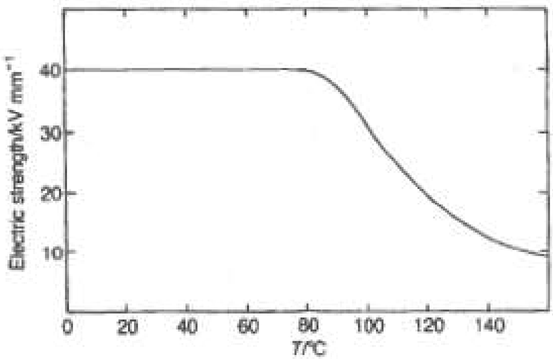
The Z_W component (Warburg impendance) is not always observed at low frequency; it depends on the interaction between electrode and dielectric

Dielectric breakdown

Dielectrics also break down under high electric fields

- Electrons start to conduct, causing localised heating and breakdown
- This is quantified as the **Dielectric Strength** (in *e.g.* V m^{-1})





How good is a capacitor for energy storage?

Take *e.g.* a $BaTiO_3$-based capacitor:

- $\varepsilon_r \approx 1000$
- Dielectric strength ≈ 10 MV m^{-1}
- Thickness ≈ 1 μm

Assuming a total volume of 5 cm^3 (similar to an AA battery):

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Maximum voltage = $10 \times 10^6 / 1 \times 10^-6 = 10\ \mathrm{V}$, therefore:

$$Q = CV = 0.4427\ \mathrm{Coulombs} = 0.1229\ \mathrm{mAh}$$

This is a volumetric capacity of 24.6 mAh L^{-1}, Energy capacity = 0.245 Wh L^{-1}

This is a higher than realistic estimate due to ignoring electrodes, packaging etc. but is still less than a battery!

Why are they useful then?

Although energy capacity is worse than for batteries (often by a lot), capacitors can discharge the charge very rapidly

- A discharge current of 100 Amps can be easily achieved.

This gives a high specfic power. For the $BaTiO_3$ capacitor considered before, this gives power density approximately 1000 W L^{-1}!

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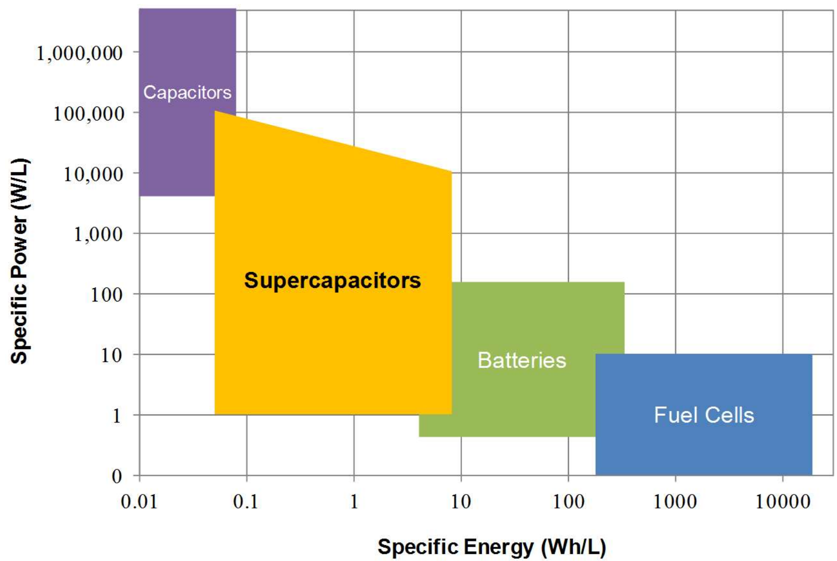

Supercapacitors

- Higher capacitance (but lower voltage limits) than other capacitors
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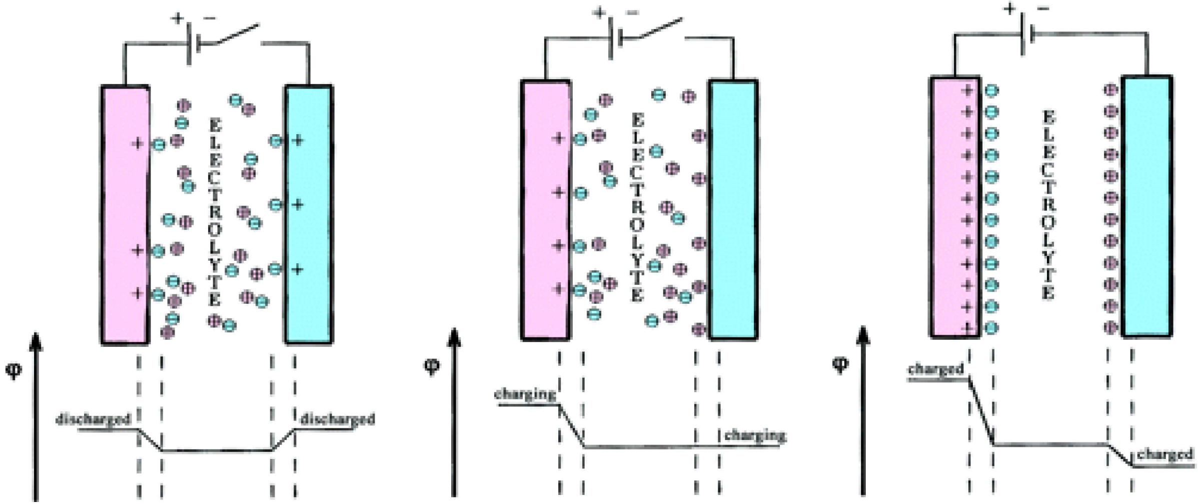
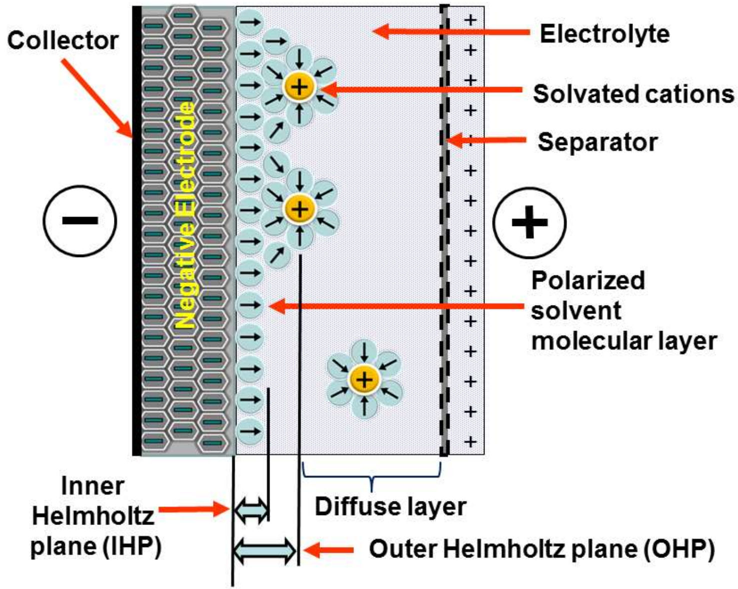
Rather than a ceramic dielectric, supercapacitors rely on an ionic electrolyte solution, and an ion-permeable membrane to prevent electronic conduction.



M. Winter, *Chem. Rev.* 2004, 4245.

Supercapacitor operation

Charge is stored in a **Helmholtz double layer** at each electrode:

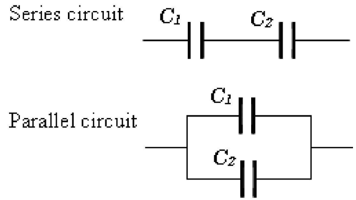


This separation of +ve and -ve charges occurs over a few angstroms

- This is effectively a capacitor with very small *d*

Capacitance

Because there are two double-layers, a supercapacitor behaves as two capacitors connected in series:



$$\frac{1}{C} = \frac{1}{C_a} + \frac{1}{C_c}$$

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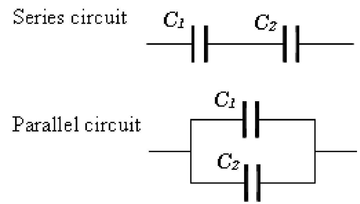

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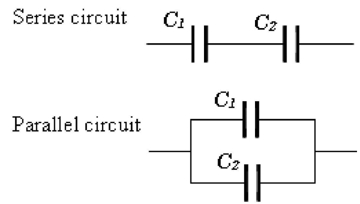

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For a symmetric supercapacitor (commonly called ultracapacitor, where anode and cathode are the same material):

$$C = \frac{C_A}{2}$$

The total energy stored is:

$$E = \frac{QV^2}{2}$$

Charging voltages are typically 1-3 V (depending on electrolyte).

Electrolytes

Aqueous

- Acids (*e.g.* H_2SO_4)
- Alkalis (KOH)
- $NaClO_4$ or $LiClO_4$
- $LiAsF_6$

Organic

e.g. acetonitrile, propylene carbonate, tetrahydrofuran with:

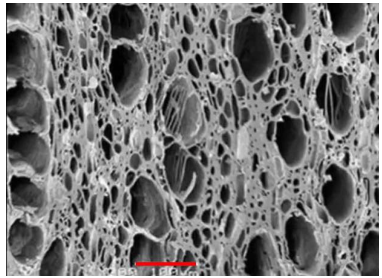
- Tetraethylammonium tetrafluoroborate, $N(Et)_4BF_4$
- Triethyl(methyl) tetrafluoroborate, $NMe(Et)_3BF_4$

Electrode materials

$C \propto$ amount of double-layer $\propto A \rightarrow$ electrodes are designed to have maximum area

Porous (activated) carbon

- Surface area exceeding 3000 $m^2\ g^{-1}$
- Trade-off between surface area and pore size
    - Smaller pores limit maximum current (power density) but increase energy capacity



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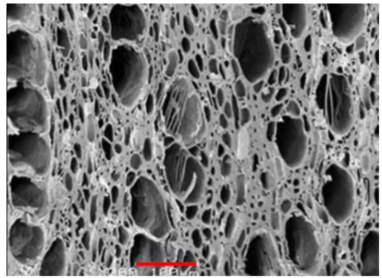
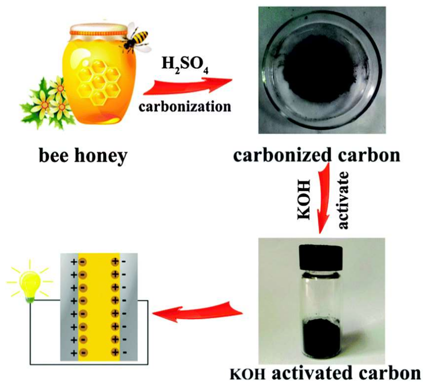
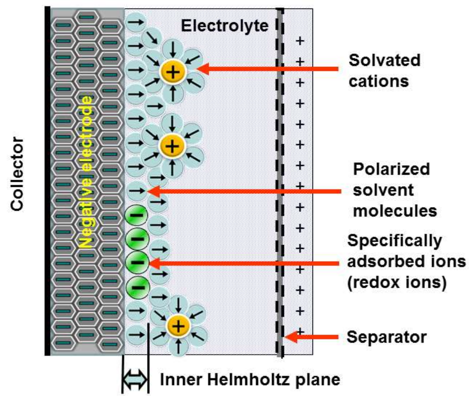
- Activated carbon is relatively expensive and potentially unsustainable
    - High temperatures and aggressive chemical activation required
    - *Biochar* (a by-product of biofuel production) is one alternative





Pseudocapacitance

One way to increase energy storage in supercapacitors is to add redox-active species.



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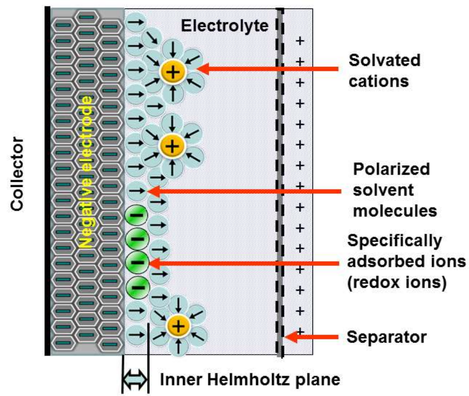

- Must be fast, reversible redox processes (so that power density remains high)
- Pseudocapacitance can contribute 100 times the double-layer capacitance
- Redox ions must have affinity for the electrode(s)
  - MnO_2 is commonly used as an electrode

NOTE: In order to be considered pseudocapacitance, charge stored must depend linearly on the applied voltage (otherwise it is behaving like a battery)

T. Brousse, *J. Electrochem. Soc.*, 2015, A5185

Hybrid technologies

One of the main drawbacks of supercapacitors is that their voltage drops with time

- Not ideal for powering devices

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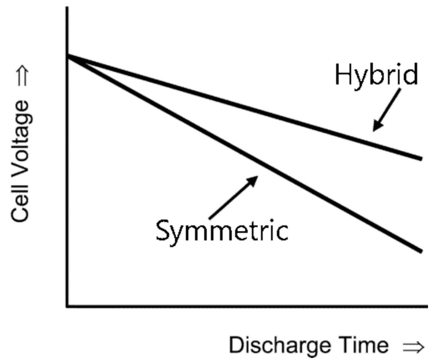
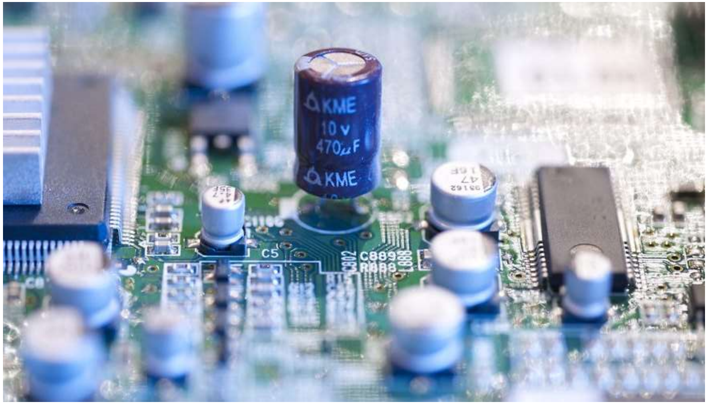
Hybrid capacitors combine a battery-electrode with a supercapacitor electrode

- *e.g.* replace carbon cathode with NiOOH
- $C_{battery} \approx 10 \times C_{supercap}$
  - $\frac{1}{C} = \frac{1}{C_A} + \frac{1}{10C_A} \approx \frac{1}{C_A}$
- In some cases (*e.g.* thin-film Li electrodes) fast redox kinetics still allow high power applications



(Super) Capacitor applications



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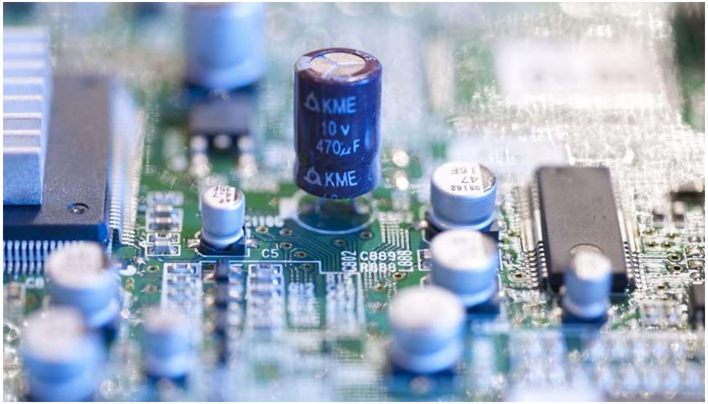

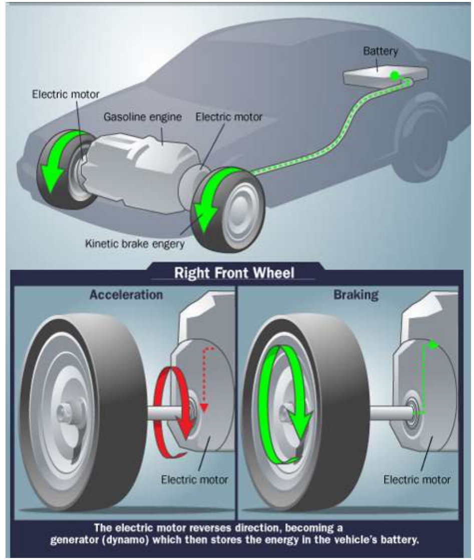

Regenerative braking

- Recovers kinetic energy lost when braking
- Large currents generated; supercapacitors required to store charge

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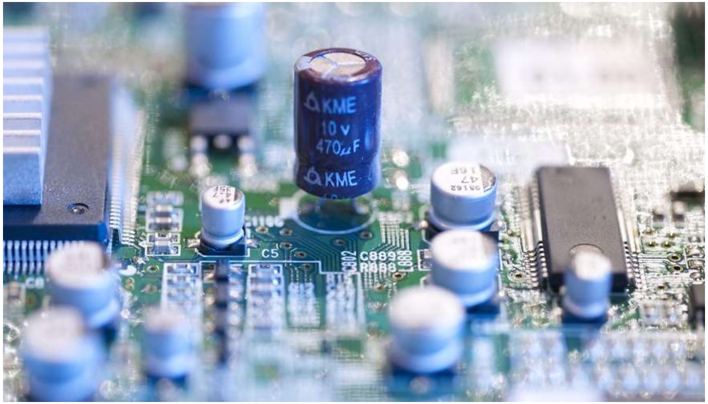

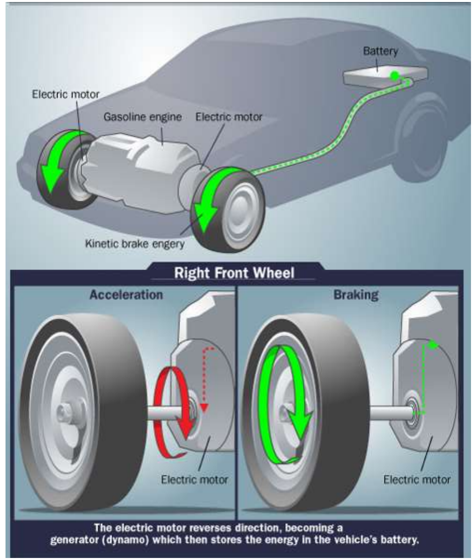

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Medical devices *i.e.* pacemakers

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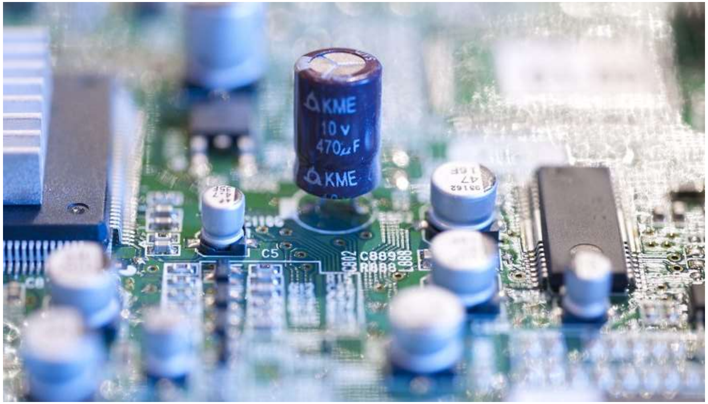

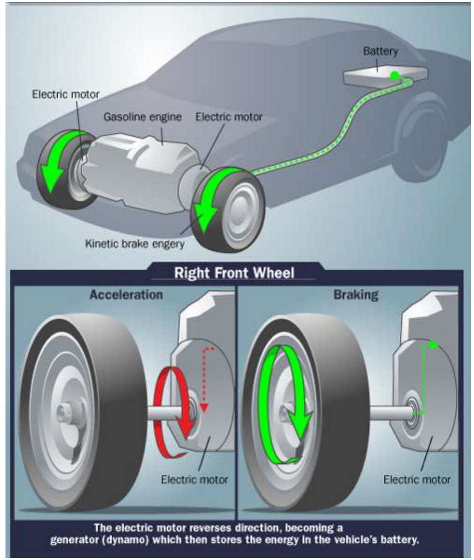

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