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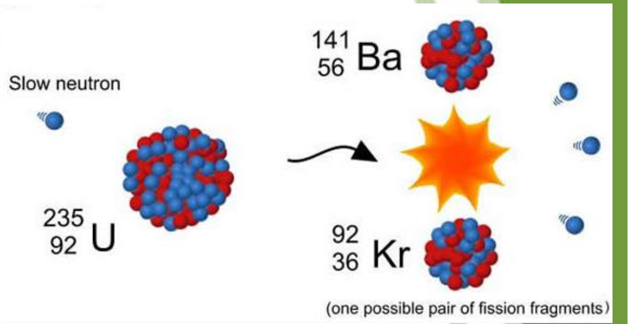
Basics of Energy Storage Devices

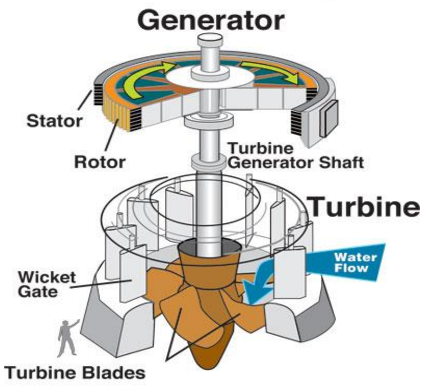
Imran Shakir

Introduction









Today, we can convert energy from many different forms into usable electricity.

But how did we get here ?

In ancient times, the generation of electricity was purely accidental.

1. Drag feet on carpet
2. Pet a cat
3. Take off a sweater

By rubbing certain materials together, static charges can be accumulated

Ancient Greeks rubbed amber on fur to generate electricity. In fact, the word elektron comes from the Greek word for amber By the mid 1600’s, static electricity could be readily generated by rubbing insulating materials together: fur/cloth, sulfur, amber, etc.

Background

But the main problem for electricity is how we store it from the generation source?

Background

But in the 1600's, scientists did not really know much about electricity or how to use it. The spark generators were mostly used by scientists to study the nature of the sparks

In 1745 (Musschenbroek and Cunaeus)

Glass filled with water and get a shock by touching a metal nail

Simplified version

Metal foil wrapped around the inside and outside of a jar with a chain connecting the inner layer

Lyden Jar – Named after a city Lieden

First Capacitor

We know these devices as capacitors, but they work by storing charge ELECTROSTATICALLY

Introduction

Although they still didn't know all that much about electricity, they now had methods of storing and generating electricity, but it was still a research tool.

In fact, this enabled many important experiments of the time.

In 1746-Nollet assembled a line of 200 monks each holding the end of a wire to test if electricity can travel faster than human communication. Without warning he connected a Leyden Jar to the ends …

Background

1747-1753 Cavendish used Leyden Jars to discover many of the fundamental physics laws of electricity
Inverse square law for force, electric potential, capacitance, resistance.

But Cavendish did not publish all that much and these discoveries were rediscovered years later by Faraday, Ohm, Coulomb, Maxwell

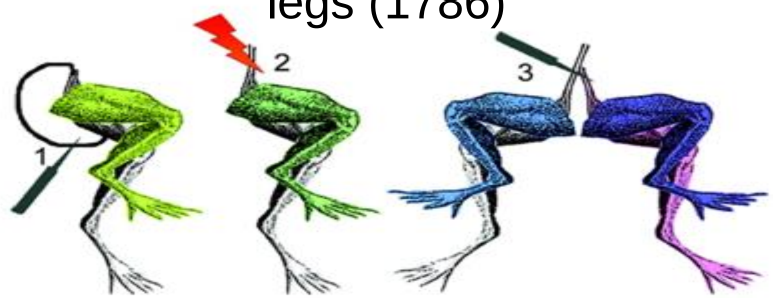
We later found out he was very wrong, but unfortunately it was too late. This is why current goes in the opposite direction of electron flow.

Kite Experiment (1752)

Franklin's other main contributions to the field include the concept of current as the flow of positive charges, and the term battery

Birth of Electrochemical Energy Storage

Galvani's famous experiments on frog legs (1786)



He took two dissimilar metals (Zn, Cu) and touched them to the ends of a dead frog's leg

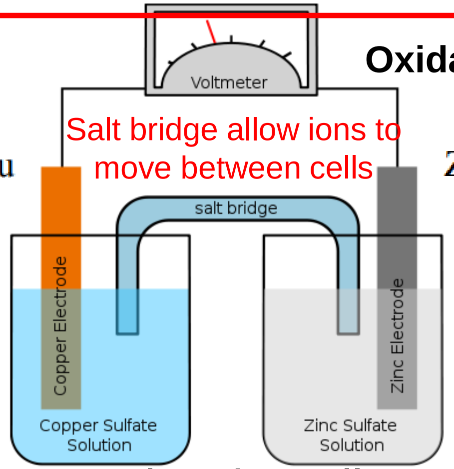
Surprisingly, the leg moved and Galvani attributed this to bioelectricity.

Reduction at cathode

$Cu^{+2} + 2e^{-} \rightarrow Cu$

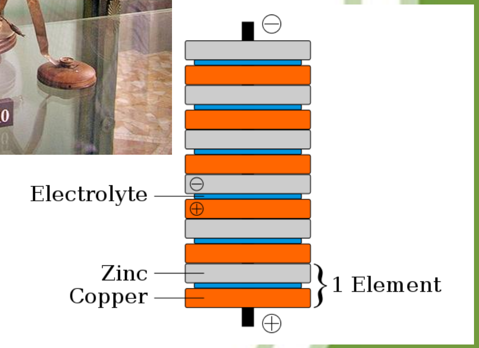
Oxidation at Anode

$Zn \rightarrow Zn^{+2} + 2\ e^{-}$



Galvanic Cell

First Battery



In 1799, Volta showed that by combining different metals that are separated by a salt or acidic solution it was possible to generate electricity

History of battery

Time	Event	Name
1791	Frog leg experiment	*Galvani*
1792	Voltaic piles	*Volta*
1820	Electricity from magnetism	*Ampere*
1827	Ohm's law	*Ohm*
1833	Ionic mobility in Ag_2S	*Faraday*
1836	$Cu/CuSO_4$, $ZnSO_4/Zn$	*Daniell*
1859	Lead acid battery	*Planté*
1899	Nickel cadmium battery	*Nernst*
1956	Alkaline fuel cell	*Bacon*
1983	Lithium metal rechargeable	*Moli*
1991	Commercial lithium ion	*Sony*

Current Needs For Energy Storage

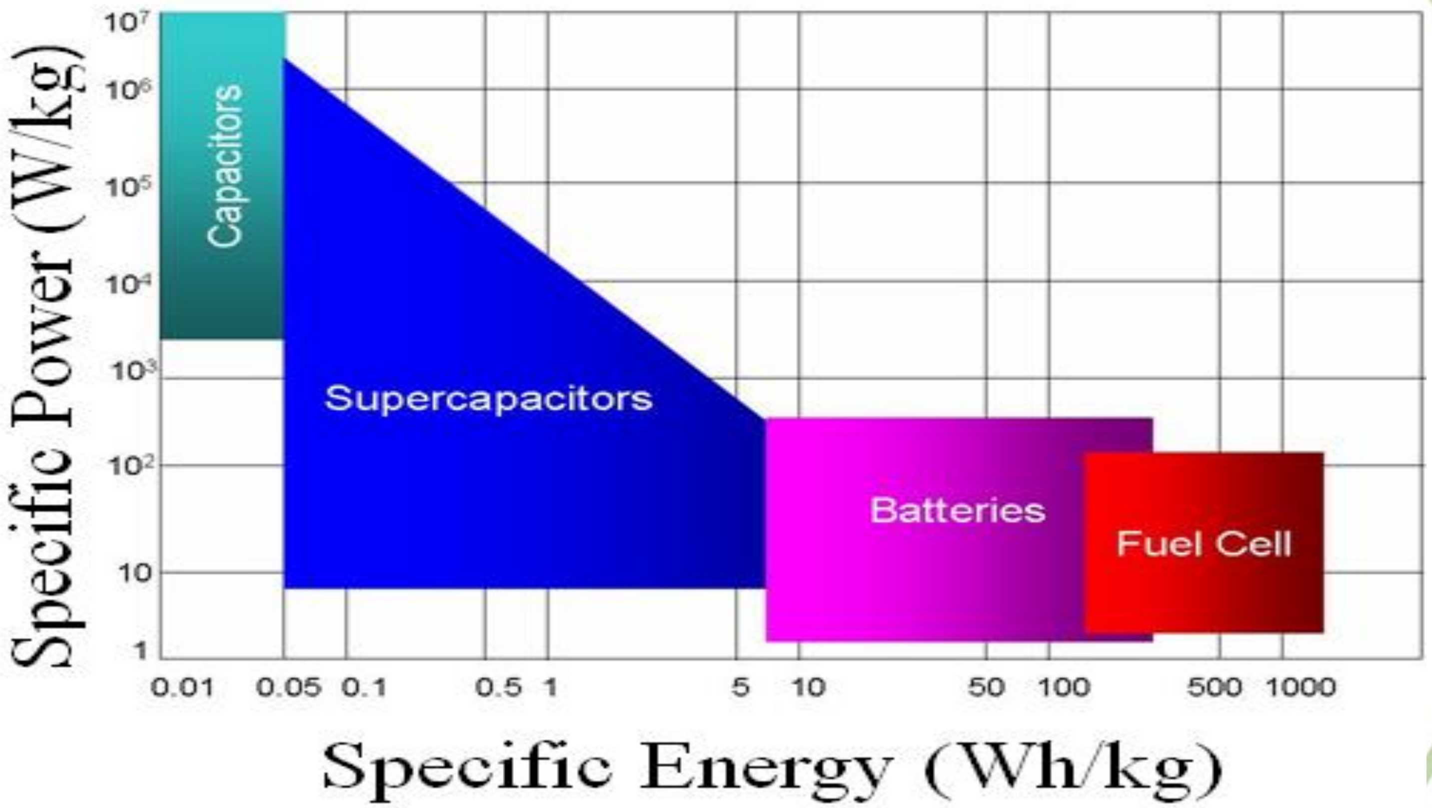
Portable Electronics

20-30% CO_2 Emission

Current Needs For Energy Storage

Large Scale Energy Storage

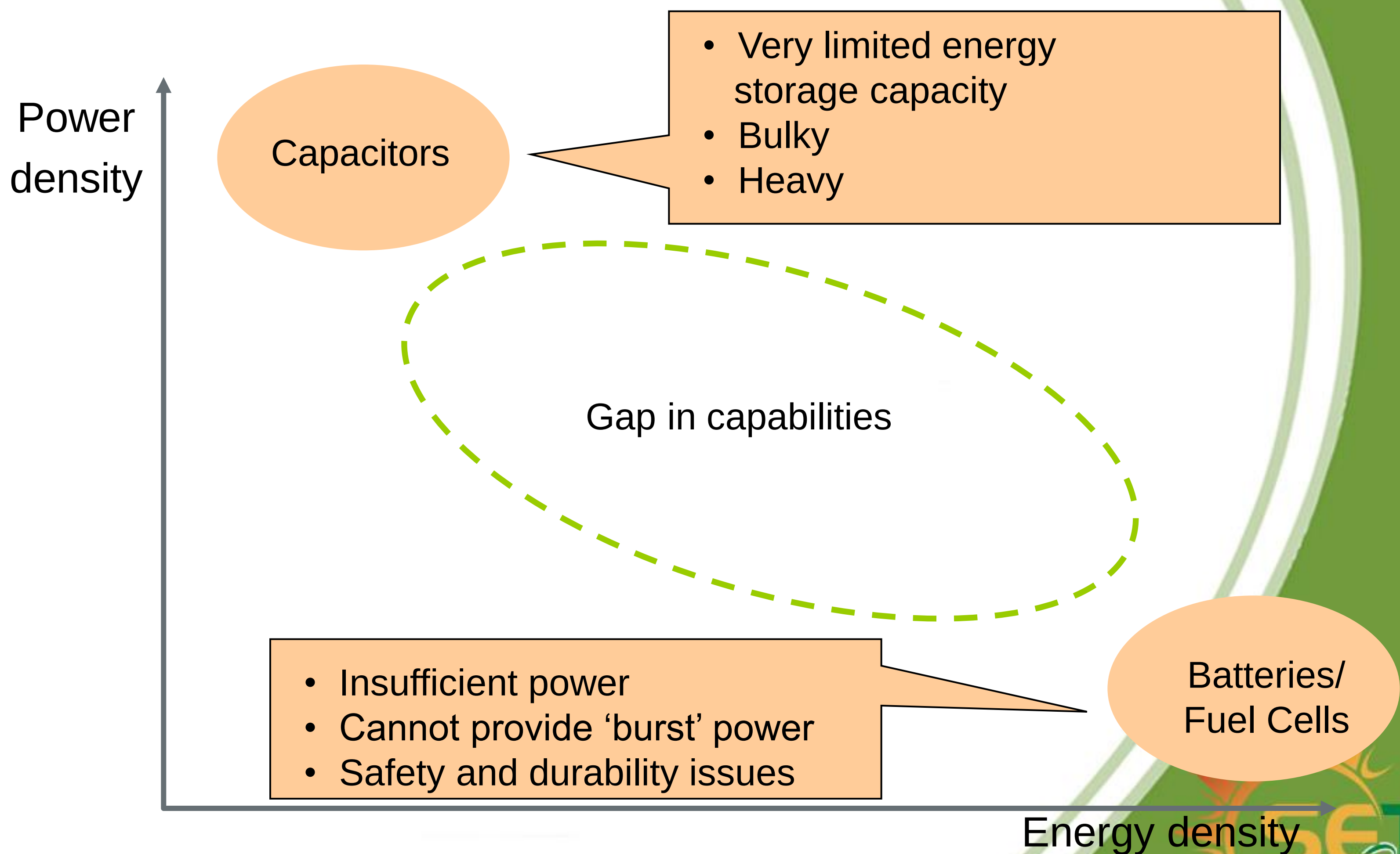
Current Energy Storage Devices



Important Parameters

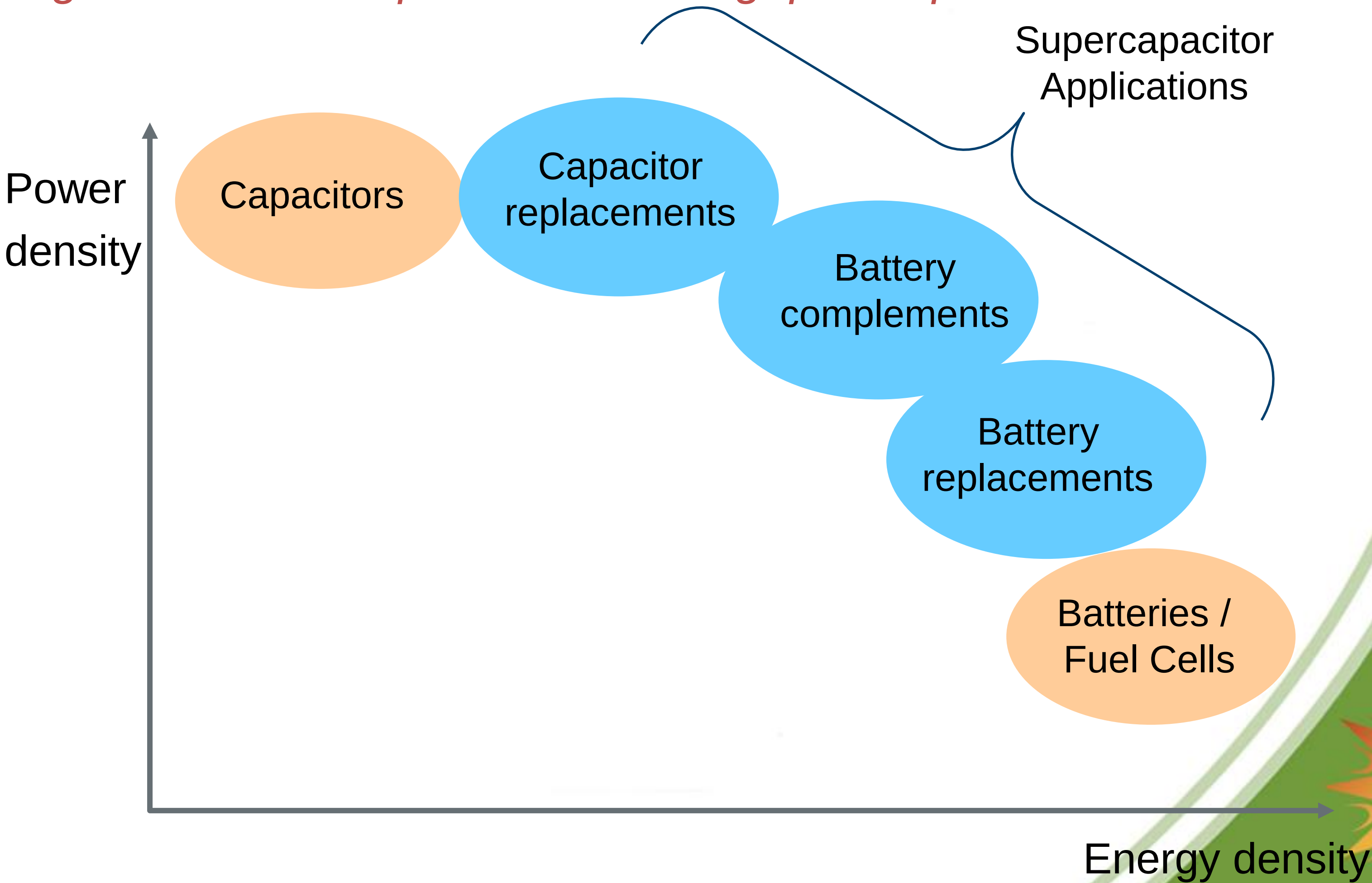
1. Energy Density (Energy per Weight or volume)
2. Power density (Power per Weight or volume)
3. Safe with long cycle life
4. Cost

Current Energy Storage Devices



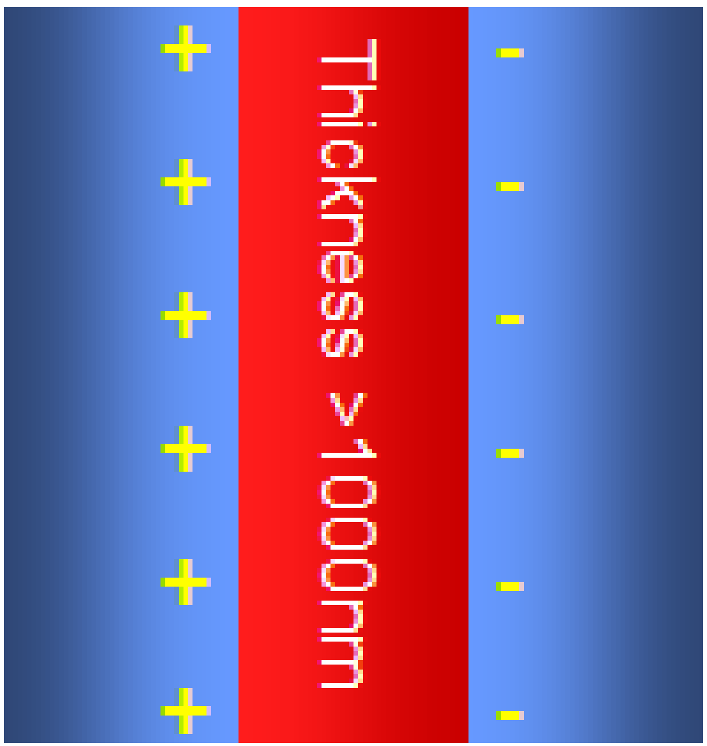
Current Energy Storage Devices

Supercapacitors have a unique ability to provide a solution that is small, lightweight and has the power to fill the gap in capabilities



Energy Storage Devices

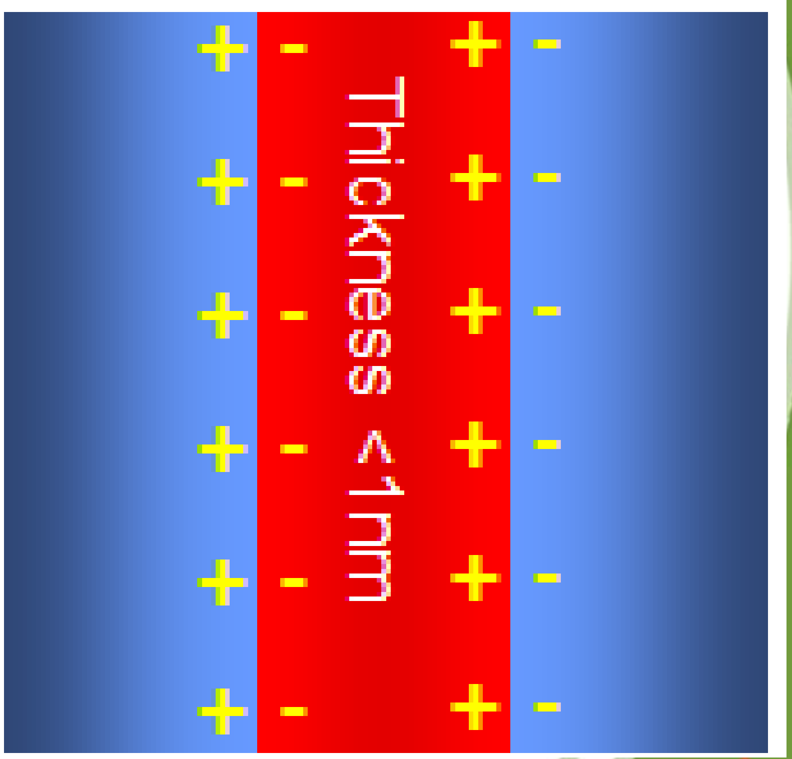
Capacitor



$C \propto 1/\text{thickness}$

$E = \frac{1}{2} CV^2$

Supercapacitor



Electrolyte solution

Energy Storage Devices

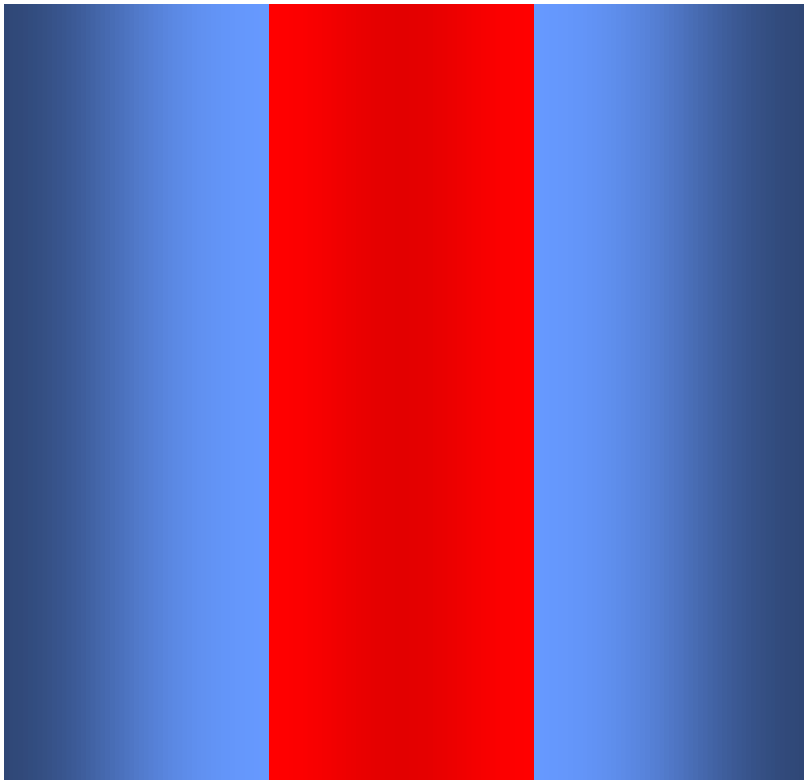
Supercapacitors – alternative way for public transport

Prototype Shanghai super-capacitor electric bus at a recharging station

Costs ~ 8000 € (after 12 years one may save 160 000 €)
Speed (max) 45 km/h
Capacity 6 Wh/kg
Distance (max) 5-9 km
Charging time 5-10 min

Energy Storage Devices

Batteries



Electrolyte solution

Capacitors and Supercapacitors are surface storage.

Battery bulk storage.

Comparison of Batteries and Capacitors

Table I – Comparison of properties of secondary batteries and electrochemical capacitors

PROPERTY	BATTERY	ELECTROCHEMICAL CAPACITOR
Storage mechanism	Chemical	Physical
Power limitation	Electrochemical reaction kinetics, active materials conductivity, mass transport	Electrolyte conductivity in separator and electrode pores
Energy limitation	Electrode mass (bulk)	Electrode surface area
Output voltage	Approximate constant value	Sloping value - state of charge known precisely
Charge rate	Reaction kinetics, mass transport	Very high, same as discharge rate
Cycle life limitations	Mechanical stability, chemical reversibility	Side reactions
Life limitation	Thermodynamic stability	Side reactions

Comparison of Batteries and Capacitors

Table II: Comparison of some important characteristics of state of the art SLI batteries and electrochemical capacitors.

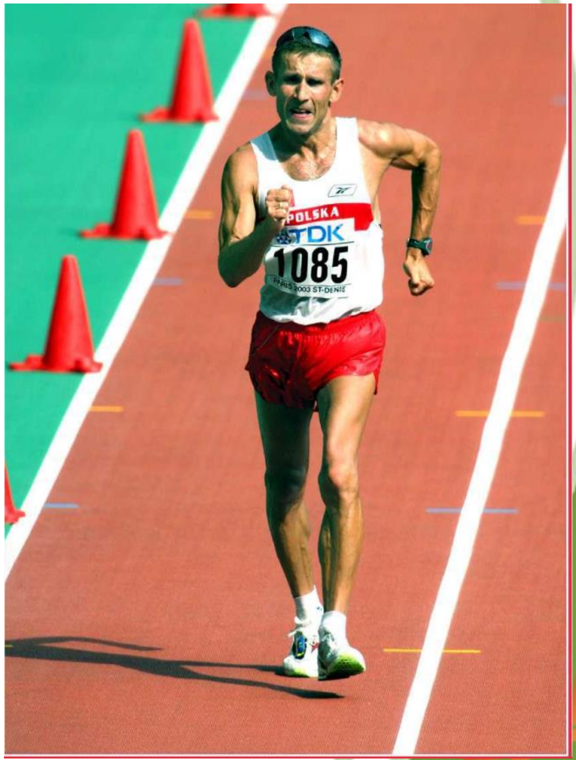
Characteristic	State of the Art SLI Battery	Electrochemical Capacitor
*Charge time	0.5-6 hour	0.3-2 second
*Discharge Time	10-30 minutes	0.3-2 second
Cycle life	200-700	>500,000
Specific Energy (Wh/kg)	25-40	1-5
Specific power (kW/kg)	0.1-0.3	5-10

* Time for discharge and charge of the useable total energy stored in the devices

Comparison of Batteries and Capacitors

Supercapacitor

Battery

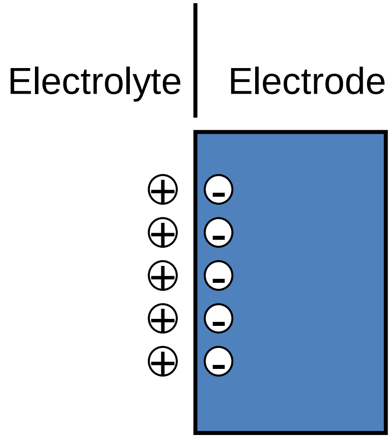


Capacitive Storage Systems

Electrochemical Capacitors

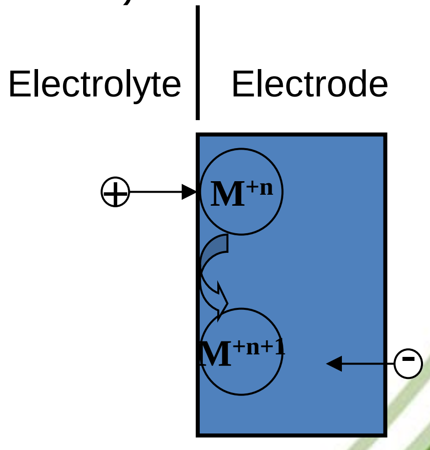
EC Double Layer Capacitor

Non-Faradaic
(no transfer of charge)

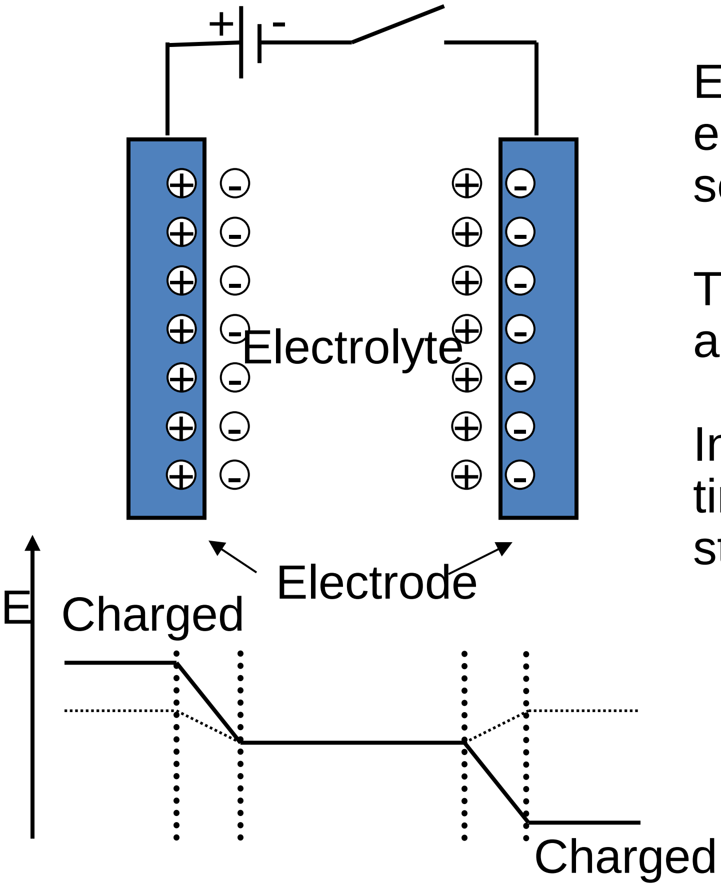


Pseudocapacitors

Pseudocapacitance
Charge transfer through surface
Faradaic, redox reactions



Electrochemical Double Layer Capacitors (EDLC)



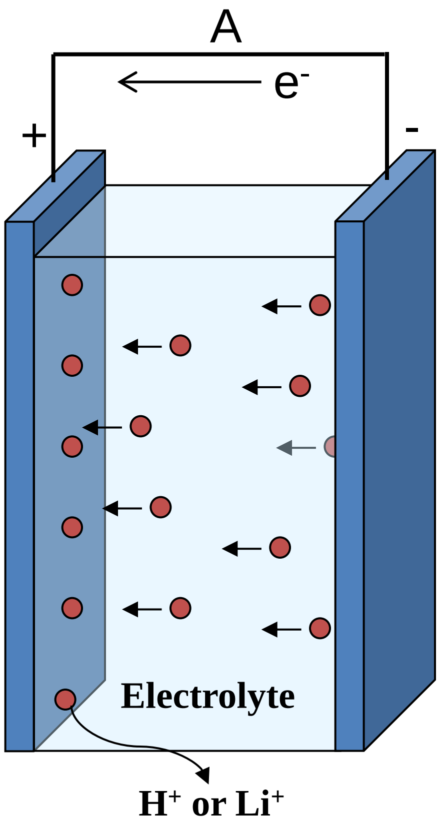
EDLCs store charge electrostatically at electrode/electrolyte interface as charge separation.

There is no charge transfer between electrode and electrolyte.

Intrinsically high power devices (short response time), limited energy storage, very high cycling stability (~10^6).

*Conway, B. E., Birss, V. & Wojtowicz, J. Journal of Power Sources 66, 1-14 (1997)

Pseudocapacitors

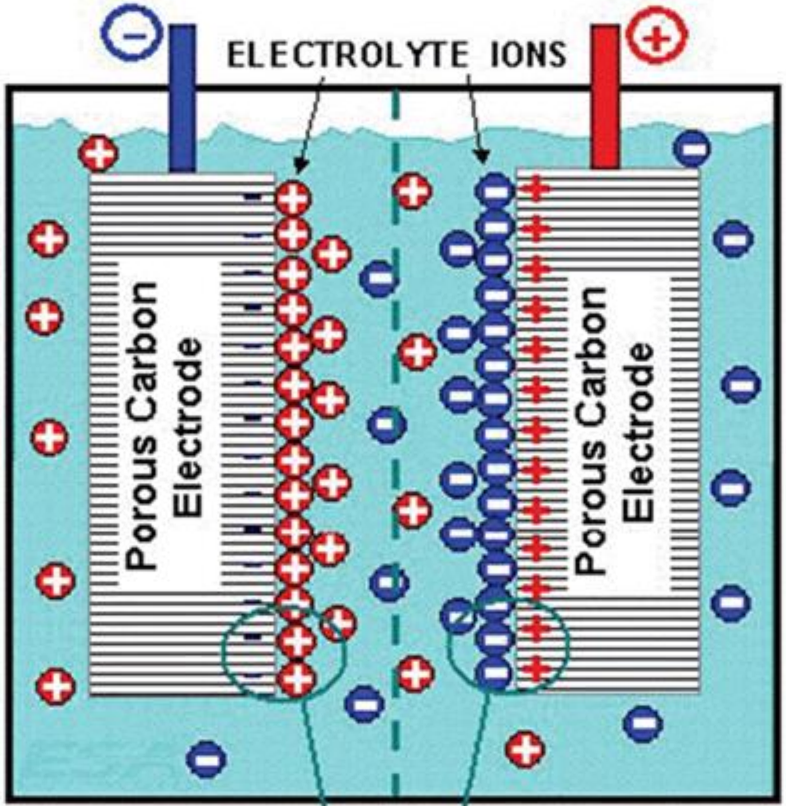


Pseudocapacitors store by charge transfer between electrode and electrolyte.

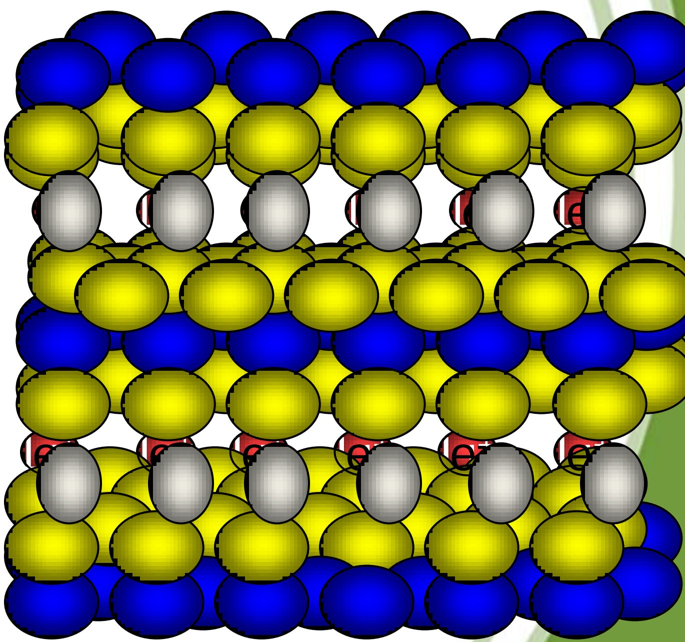
The charge is transferred at the surface or in the bulk near the surface through adsorption, redox reaction and intercalation of ions.

*Zheng, J.P., Jow, T.R., *J. Power Sources* 62 (1996) 155

Comparison

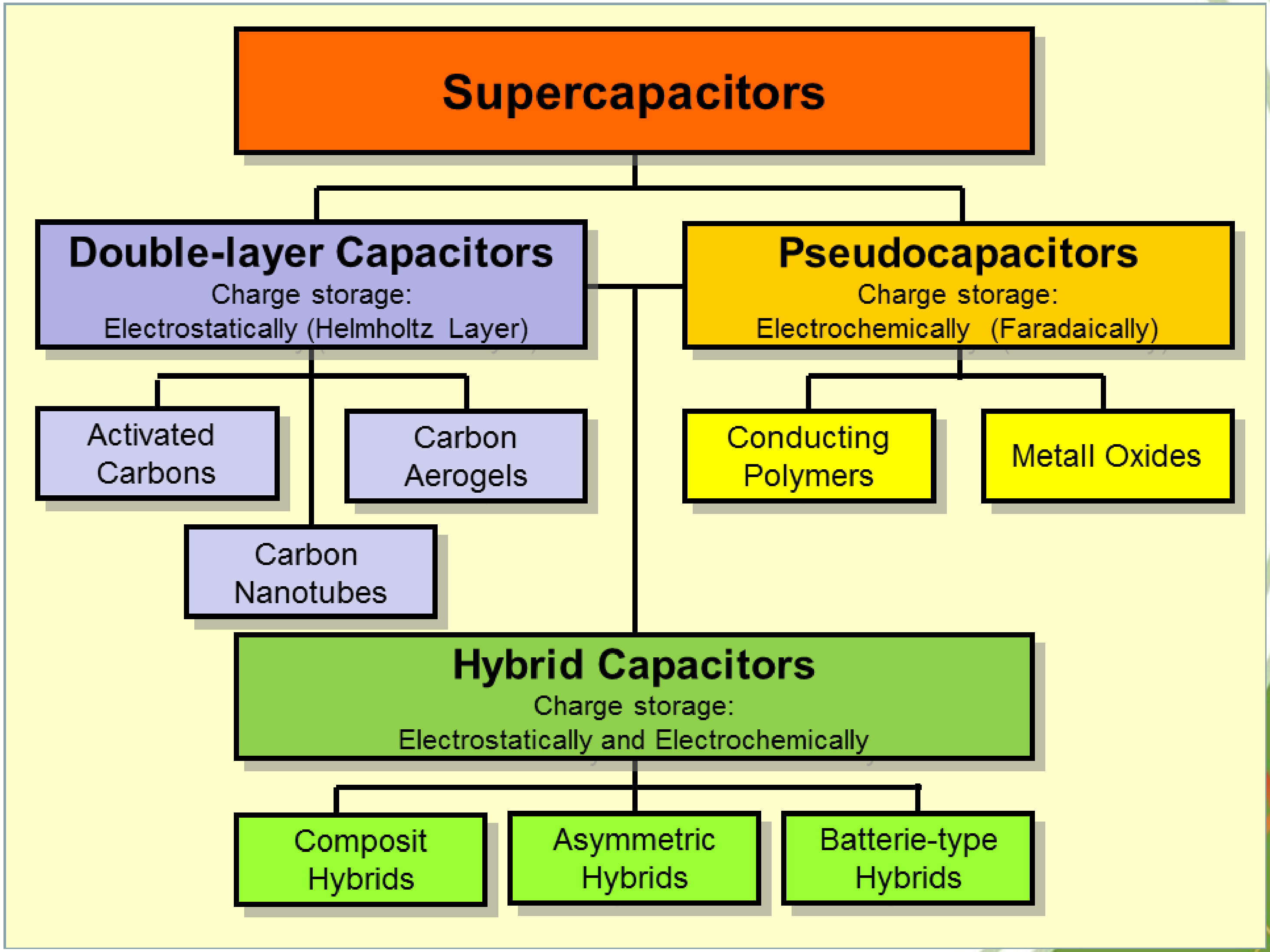


Double Layer Capacitors
(Adsorbed layers of ions and solvated ions)

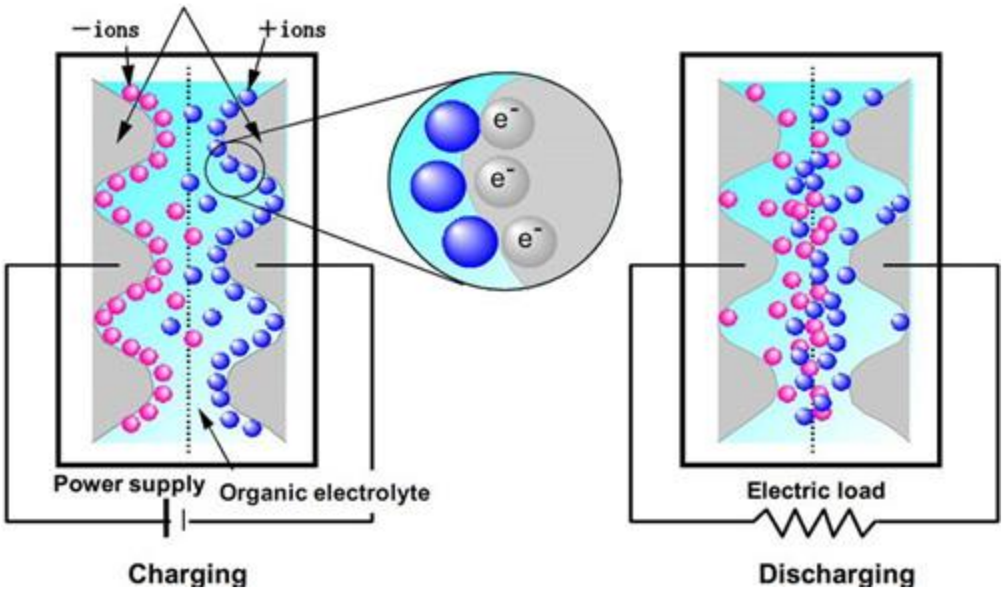


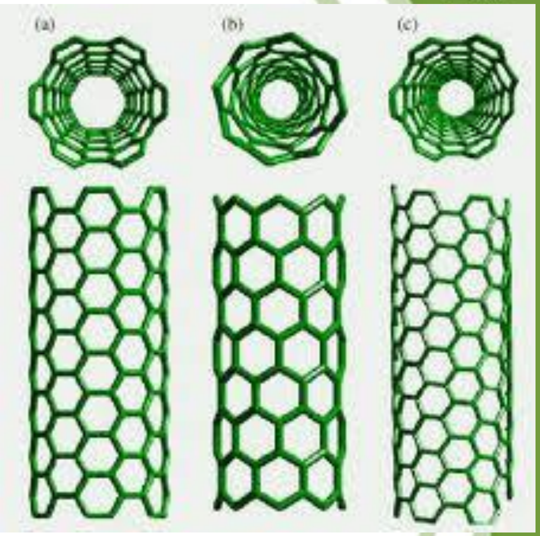
Pseudocapacitor

Materials for Supercapacitors



Double Layer Capacitors

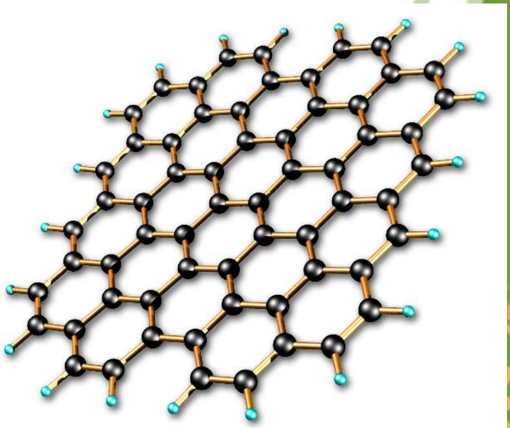




CNT_S

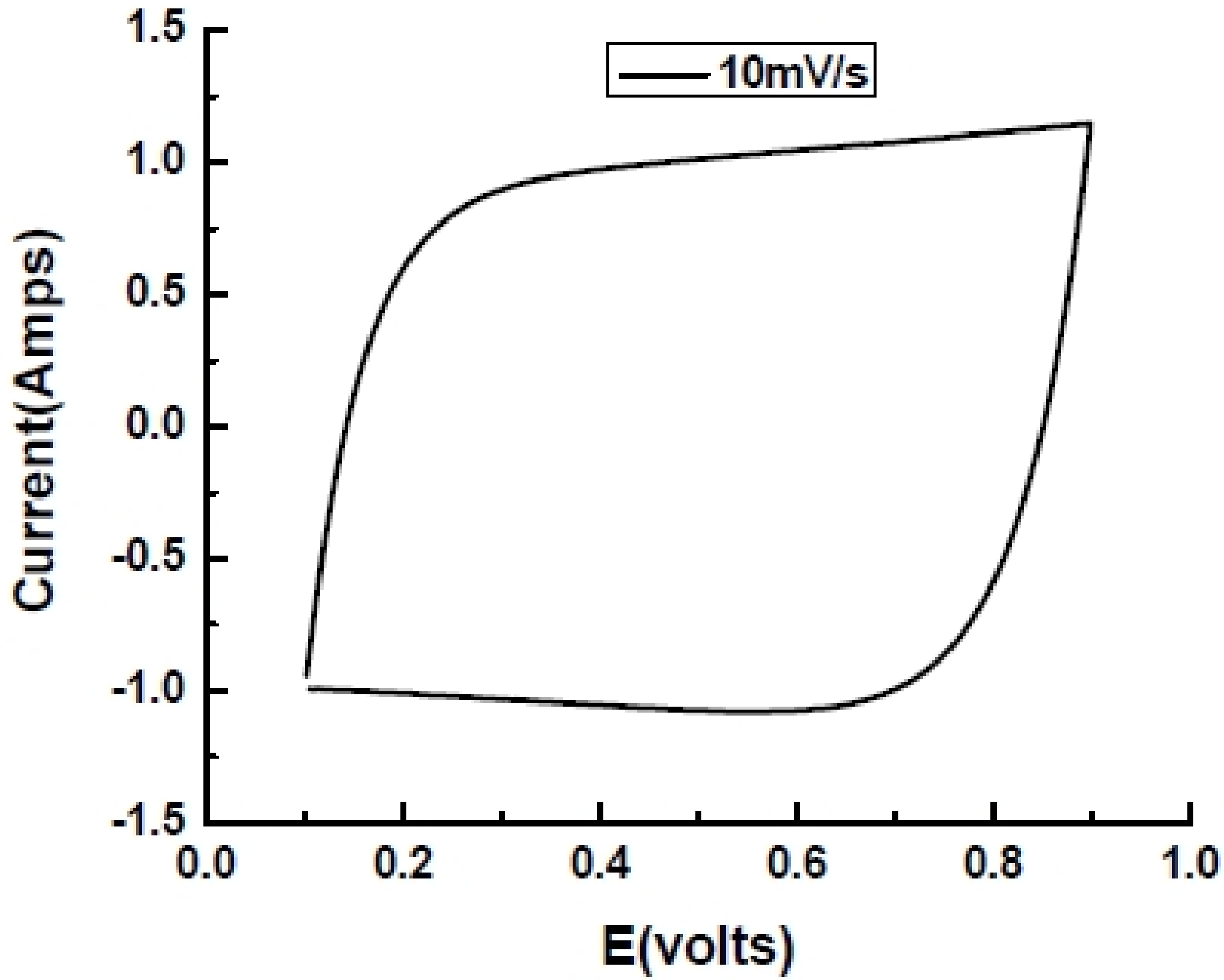
Carbon Aerogel

Activated Carbon

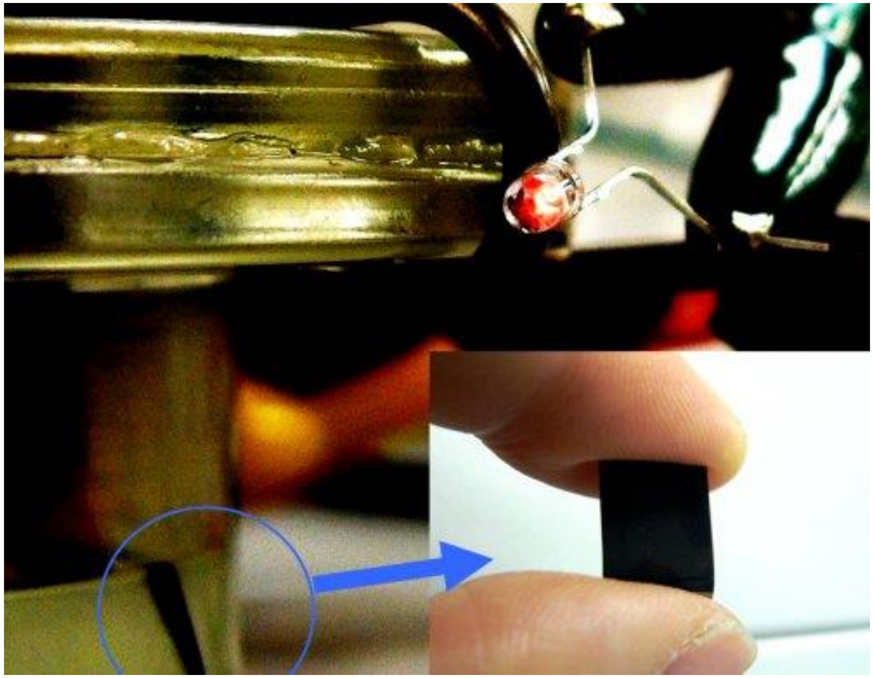


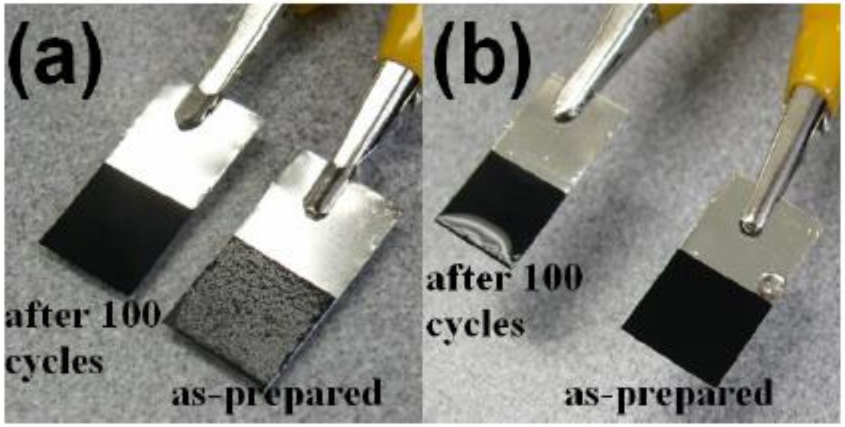
Graphene

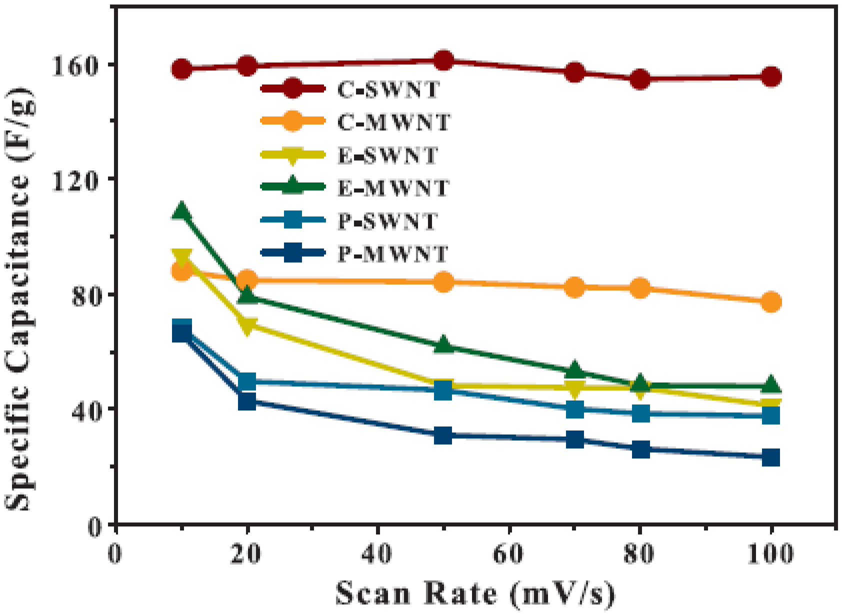
Typical CV curve for DLCs



CNTS

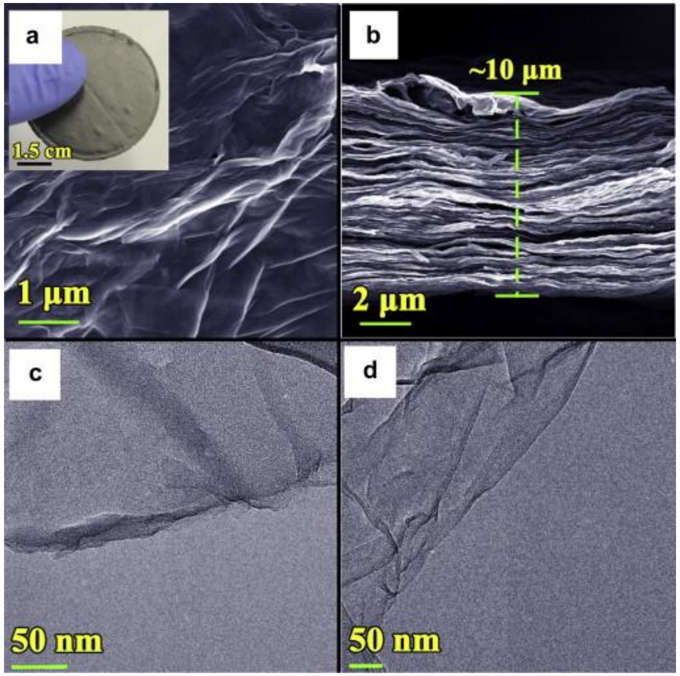


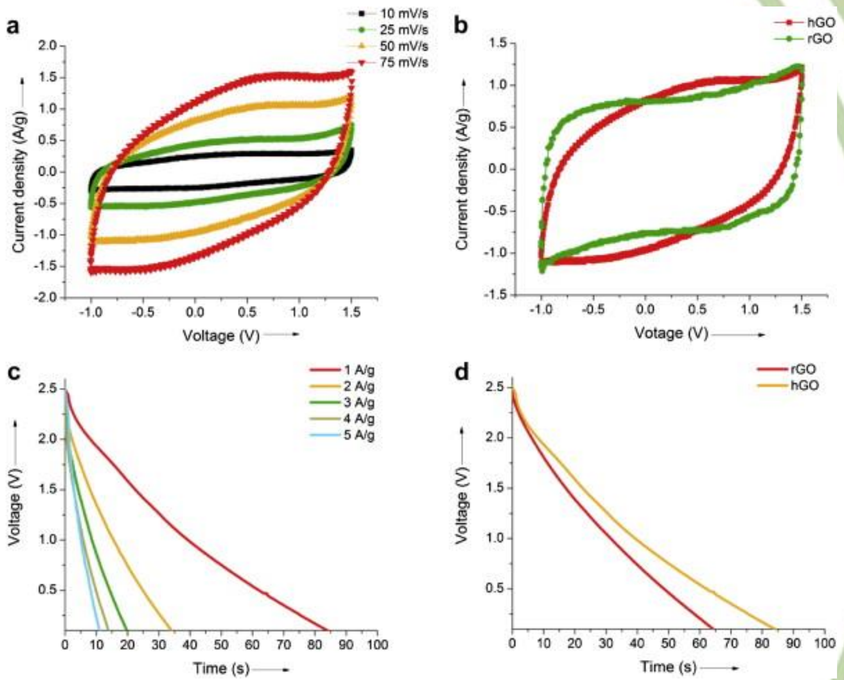


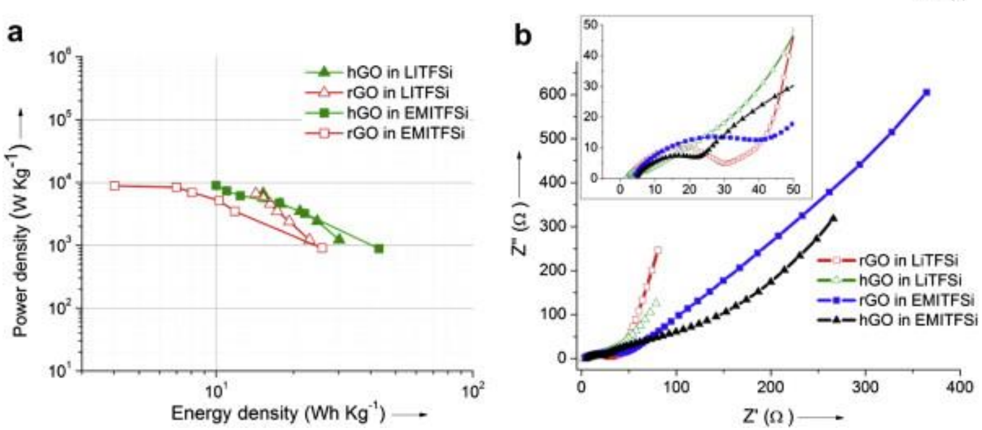


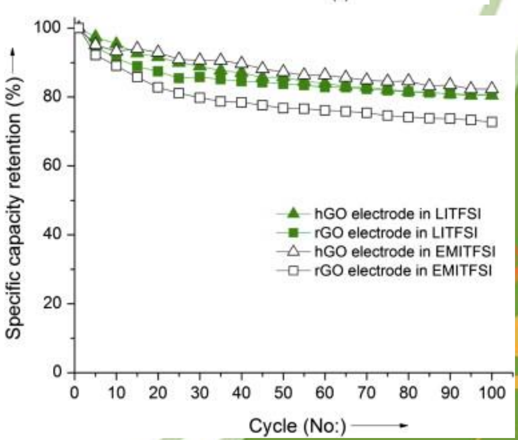
C – carboxylic
E – Easter
P - Purified

Graphene Nanosheet for EDLC

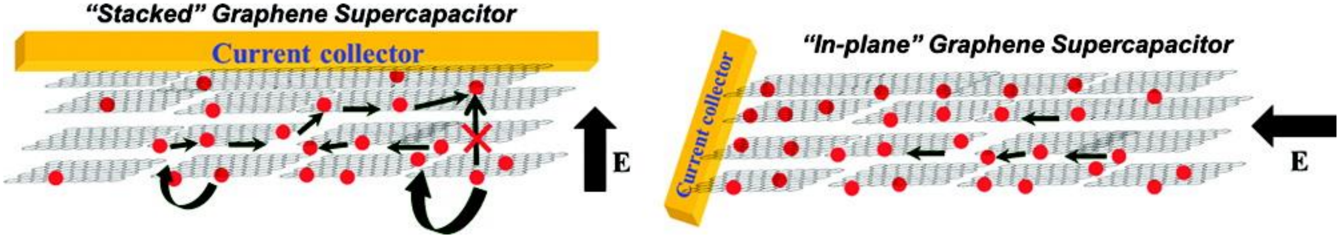


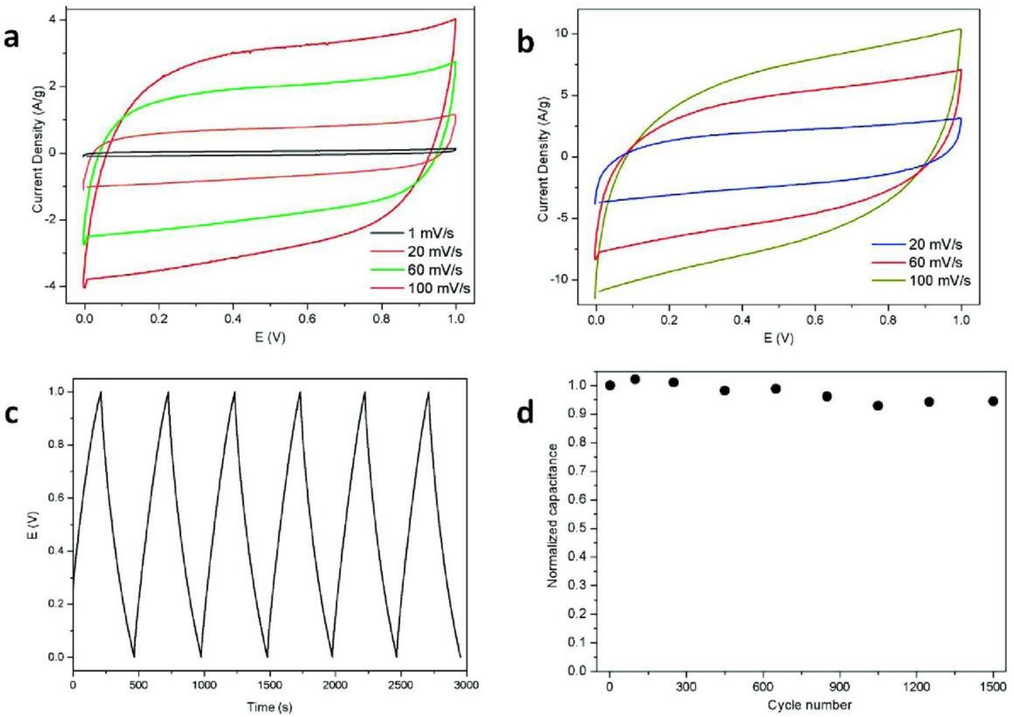






Ultrathin Planar Graphene Supercapacitors



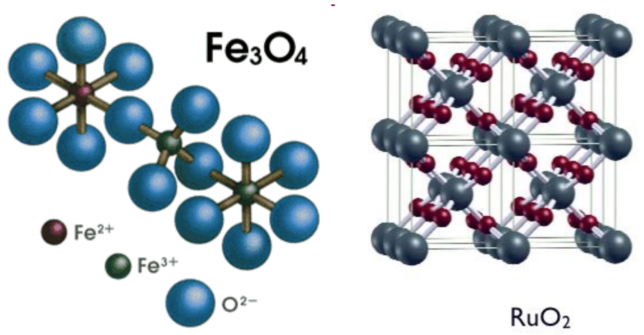


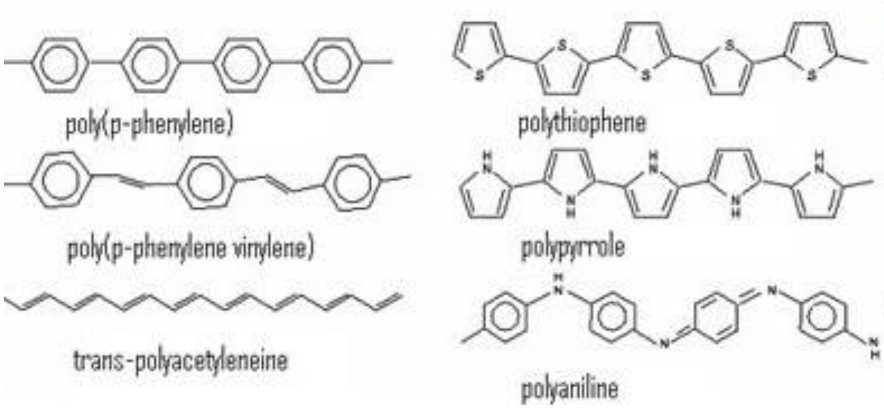
Pseudocapacitors

Store energy using fast surface redox reactions

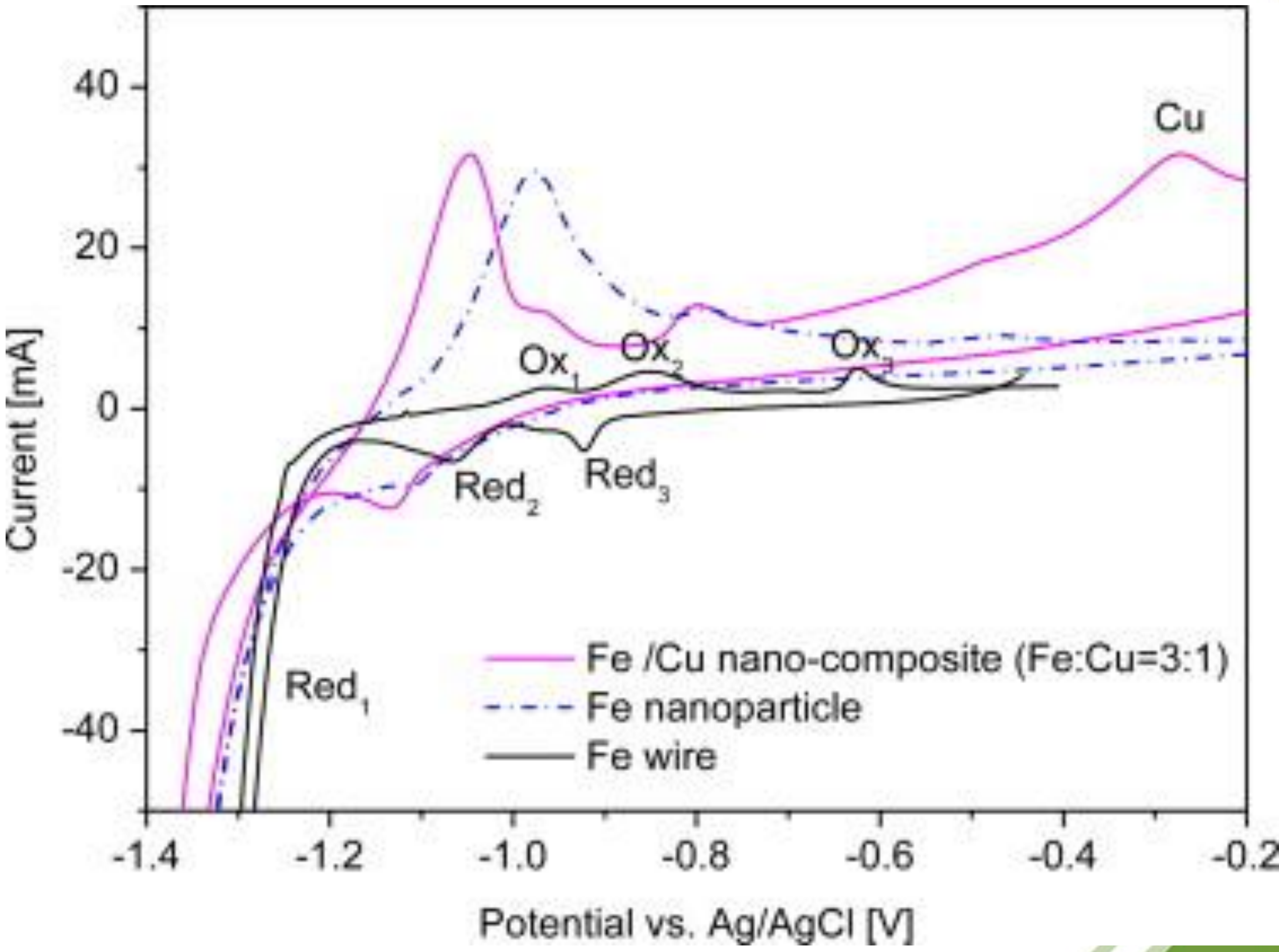
Metal oxides:
Capacity 1300 F/g (RuO_2)
Nominal voltage 1.2 V

Conducting polymers:
Capacity 30 – 40 mAh/g
Nominal voltage 1.0 V

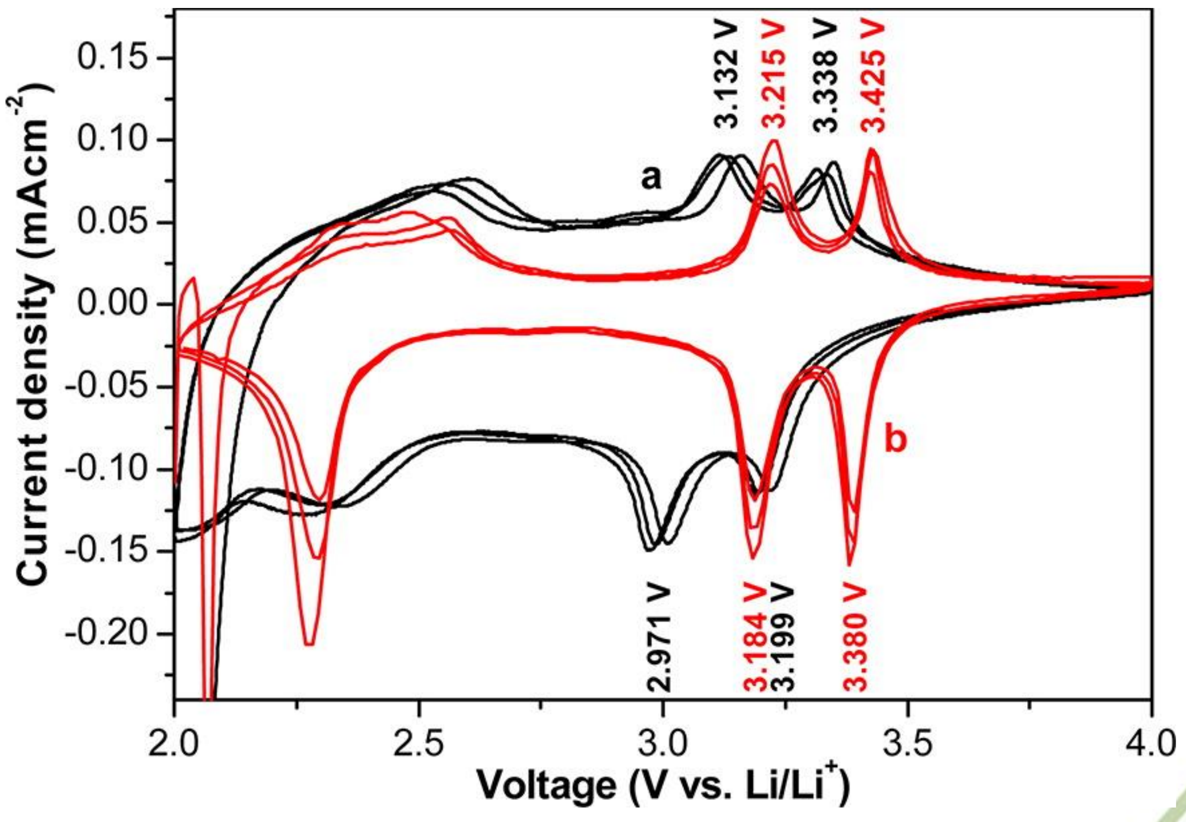




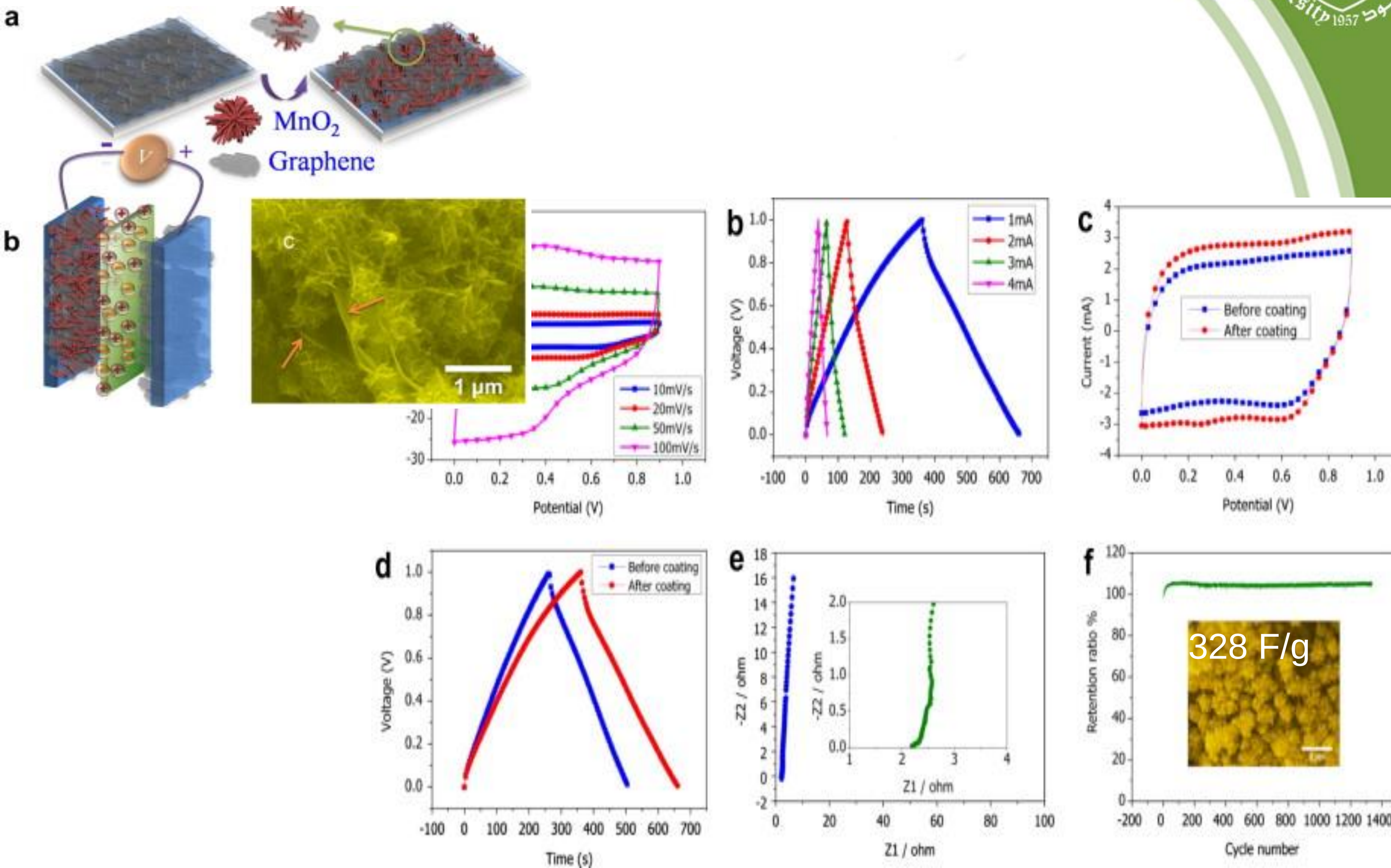
Oxidation and Reduction peaks



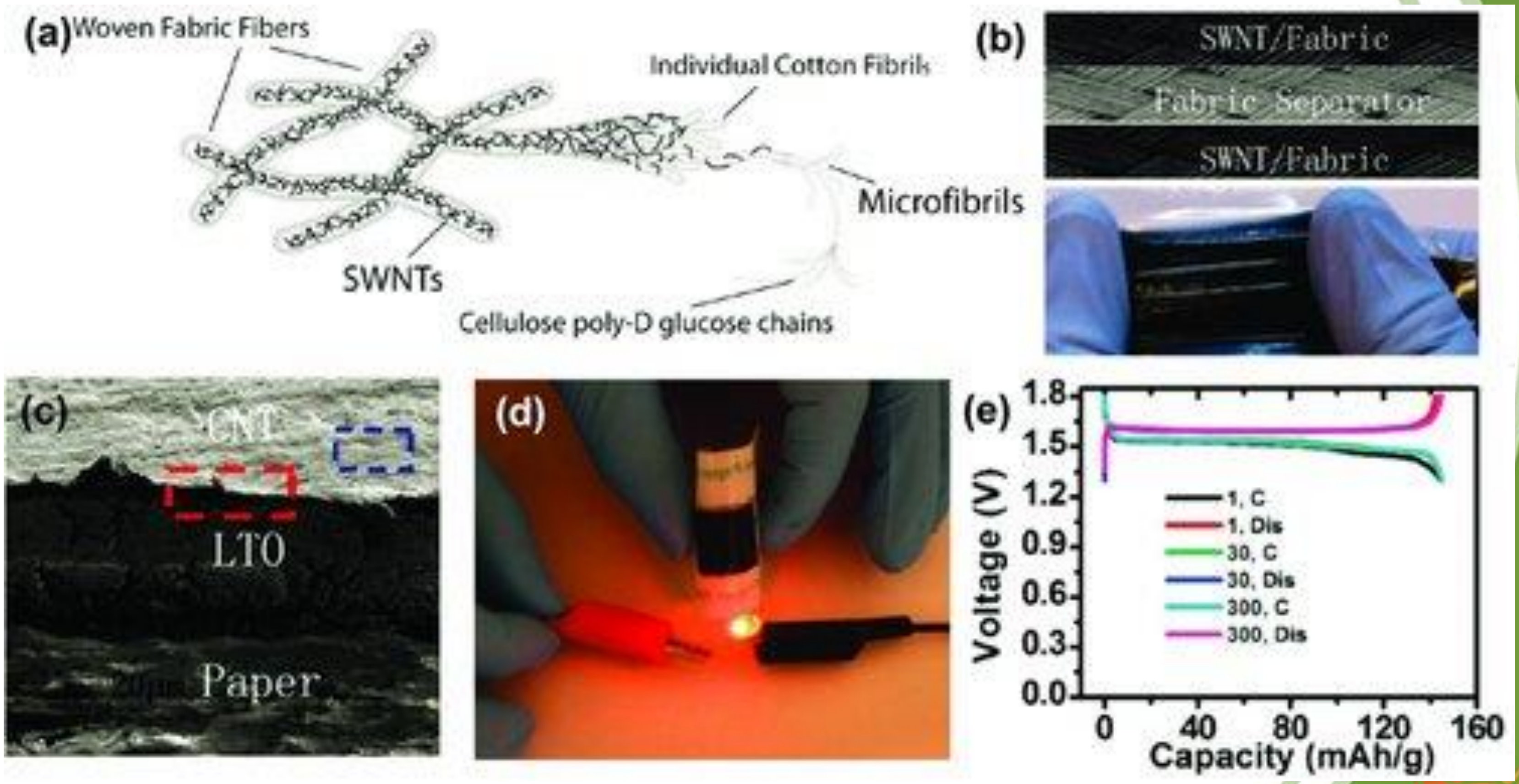
V_2O_5 a typical example



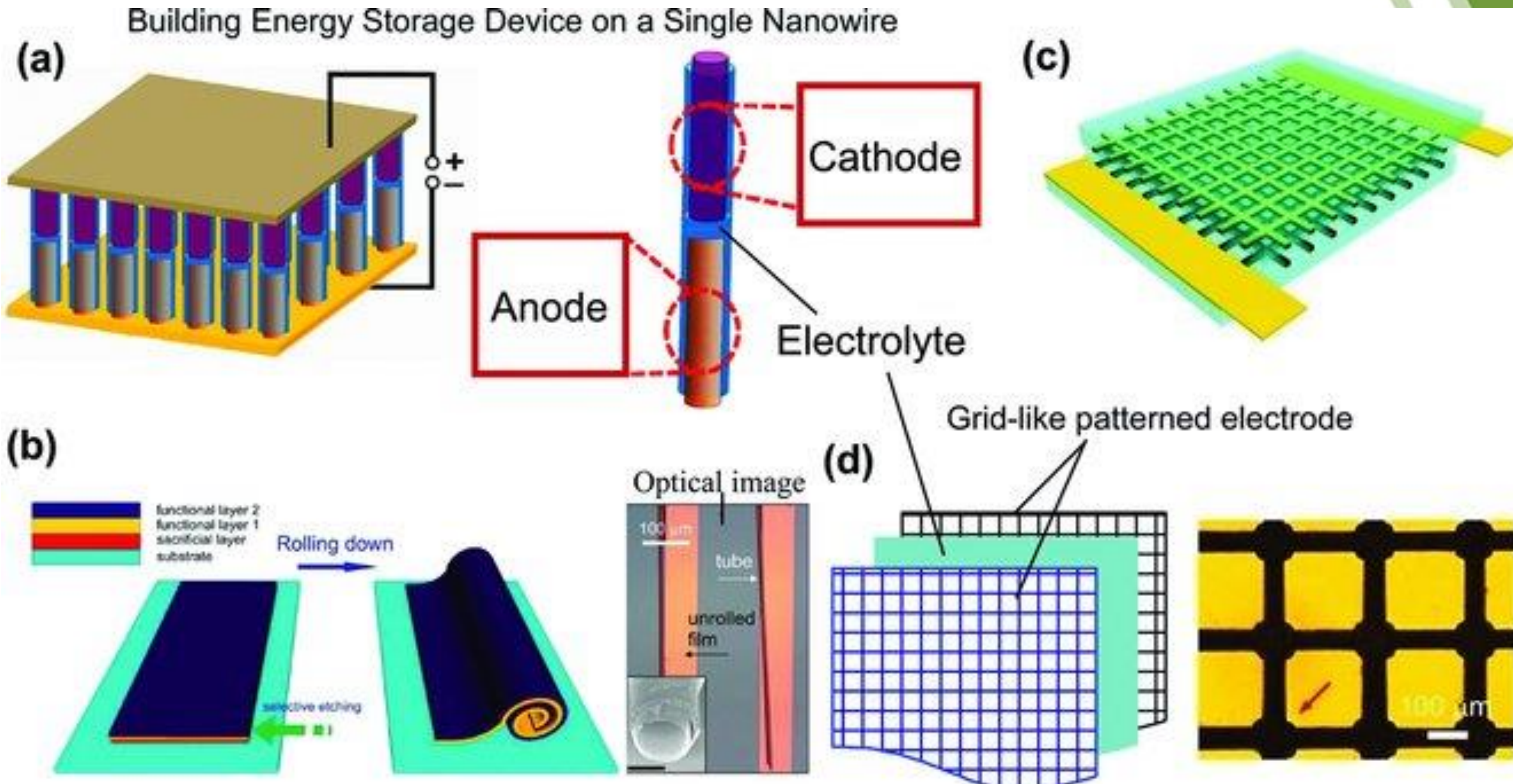
Hybrid Capacitors



Flexible paper/textile current collectors



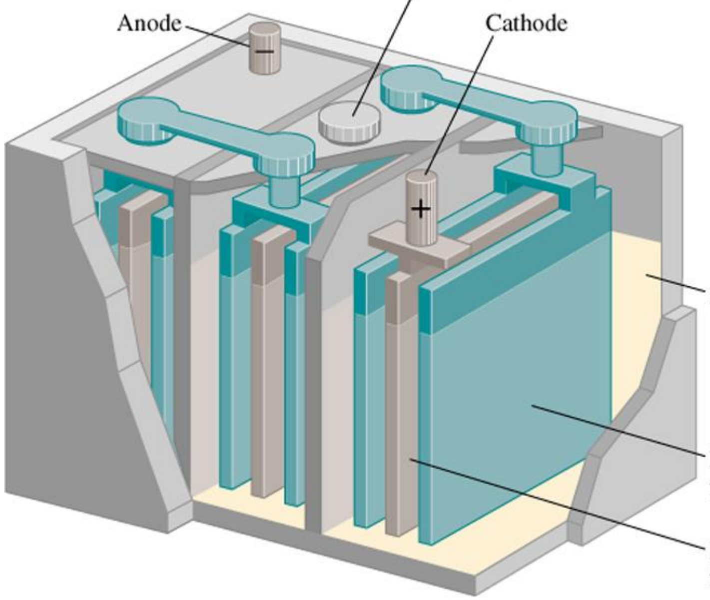
New design Architectures for Electrodes



Batteries

Lead Acid Batteries

Invented in 1859 by French physicist Gaston Planté, are the oldest type of rechargeable battery.



- ✓ Used in cars,
- ✓ Wide capability range
- ✓ Rechargeable
- ✓ Inexpensive
- ✓ Good cycle life
- ✓ Low energy density (30 ~ 40 Wh/Kg)
- ✓ Large power-to-weight ratio

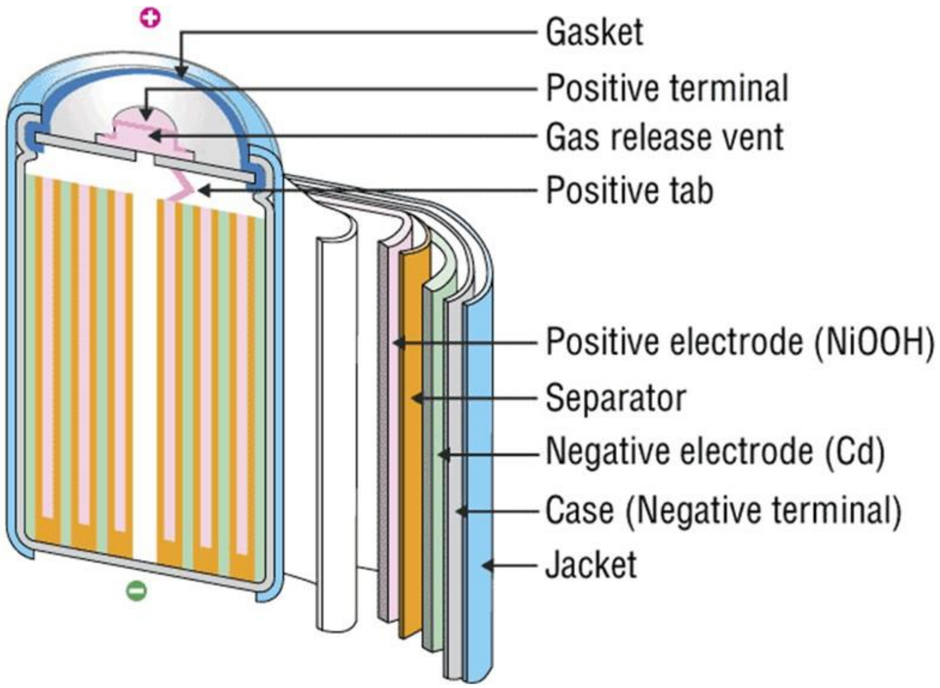
Anode: $Pb\,(s) + SO_4^{2-}\,(aq) \longrightarrow PbSO_4\,(s) + 2e^-$

Cathode: $PbO_2\,(s) + 4H^+\,(aq) + SO_4^{2-}\,(aq) + 2e^- \longrightarrow PbSO_4\,(s) + 2H_2O\,(l)$

$$Pb\,(s) + PbO_2\,(s) + 4H^+\,(aq) + 2SO_4^{2-}\,(aq) \longrightarrow 2PbSO_4\,(s) + 2H_2O\,(l)$$

Nickel-Cadmium Batteries

Wet-cell nickel-cadmium batteries were invented in 1898.



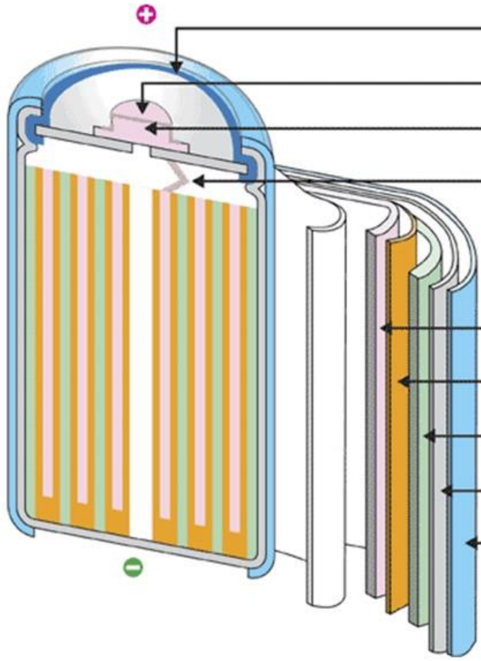
$$Cd + 2NiOOH + 4H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2 \cdot H_2O$$

$$V^o = 1.30\ V$$

- ✓ Portable appliances
- ✓ Rechargeable
- ✓ Capable of delivering exceptionally high currents,
- ✓ Can be rapidly recharged hundreds of times,
- ✓ Heavy
- ✓ Have comparatively limited energy density.
- ✓ Ni–Cd batteries are used in cordless and wireless telephones, emergency lighting, and other applications.

Nickel-metal Hydride Batteries

Battelle-Geneva Research Center developed in 1967.



- ✓ Appealing to hybrid electric vehicle
- ✓ Rechargeable
- ✓ High power density
- ✓ High energy density
- ✓ Self discharge rates
- ✓ Used in Hybrid vehicles such as the Toyota Prius, Ford Escape and Honda Civic Hybrid.

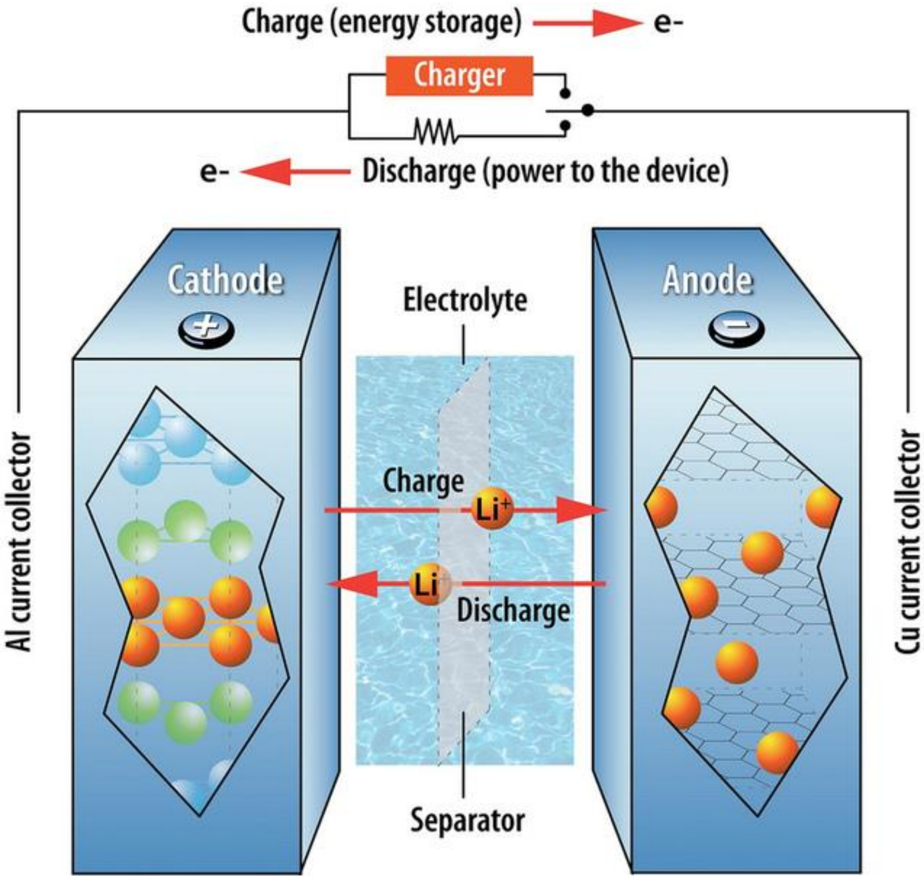
Anode: $MH + OH^- \rightarrow M + H_2O + e^-$

Cathode: $NiOOH + 2H_2O + e^- \rightarrow 2Ni(OH)_2 + OH^-$

Electrolyte: 30% KOH

Standard Batteries

- Lithium-Ion (Li-Ion)



$$C + xLi^+ + xe^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC$$

$$LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + Li^+ + xe^-$$

$$LiCoO_2 + C_6 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC + Li_{1-x}CoO_2$$

J. Mater. Chem., 19 (2009) 5871

Anode

Requirements

1) Large capability of Li adsorption
2) High efficiency of charge/discharge
3) Exellent cyclability
4) Low reactivity against electrolyte
5) Fast reaction rate
6) Low cost
7) Environmental -friendly, non-toxic

Key Requirements for Cathode

- The discharge reaction should have large negative Gibbs free energy (high discharge voltage).
- The host structure must have low molecular weight and the ability to intercalate large amounts of lithium (high energy capacity).
- The host structure must have high lithium chemical diffusion coefficient (high power density).
- The structural modifications during intercalation and deintercalation should be as small as possible (long life cycle).
- The materials should be chemically stable, non-toxic and inexpensive.
- The handling of the materials should be easy.

Electrolyte

Roles

1) ion conductor between cathode and anode
2) generally, Li salt dissolved in organic solvent
3) solid electrolyte is also possible if the ion conductivity is high at operating temperature.

Requirements

1) Inert
2) High ionic conductivity, low viscosity
3) low melting point
4) Approptiate concentration of Li salt
5) Chemical/thermal stability
6) Low cost
7) Environmental -friendly, non-toxic

Commercial electrolytes: $LiPF_6$ in Carbonate solvent

Why Li-Ion Battery?

- Lithium-Ion (Li-Ion)

Advantages

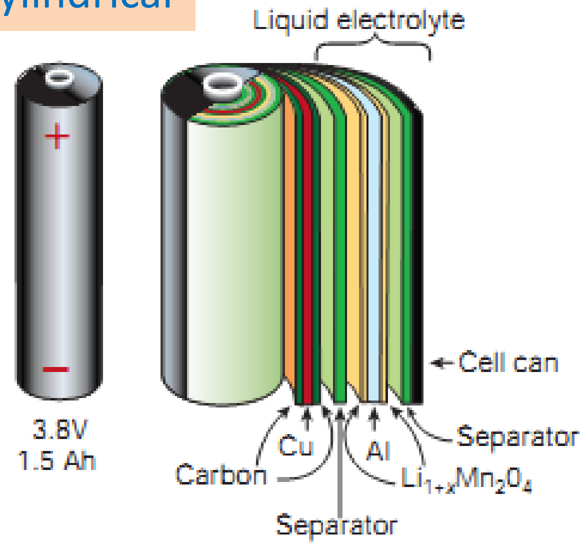
- ✓ Li has greatest electrochemical potential
- ✓ Lighter than others
- ✓ Shape and size variation
- ✓ High open circuit voltage
- ✓ No memory effect
- ✓ Low discharge rate 5-10%.

Disadvantages

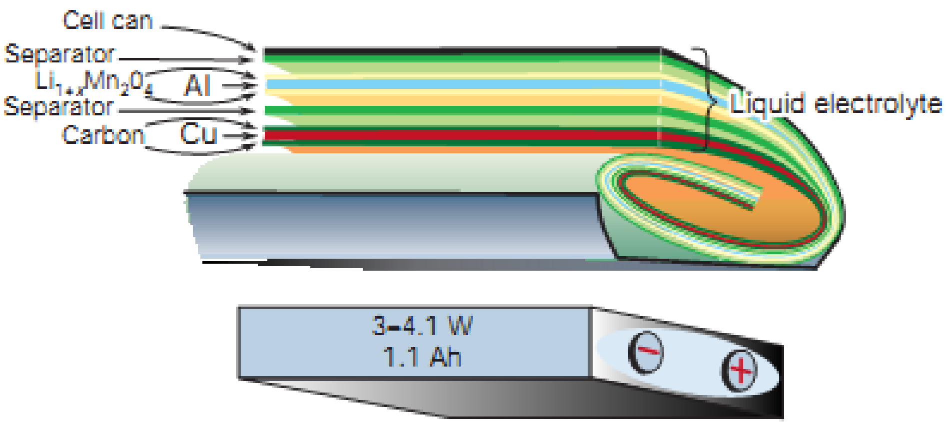
- ✓ Internal resistance is high
- ✓ Due to overcharging and high temperature capacity will diminish.
- ✓ Expensive

Different types of Lithium Ion Battery

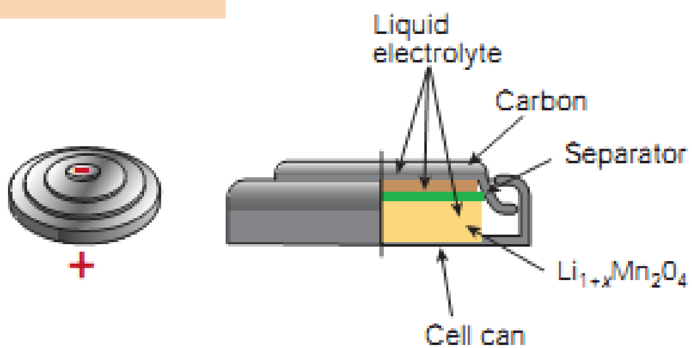
Cylindrical



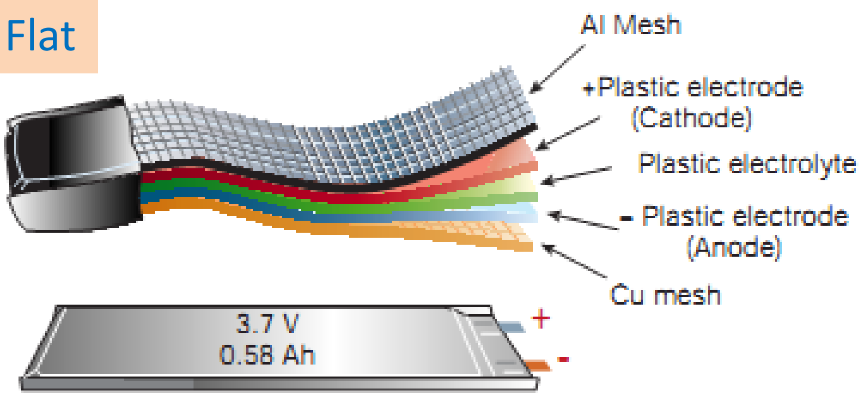
Prismatic



Coin



Thin & Flat

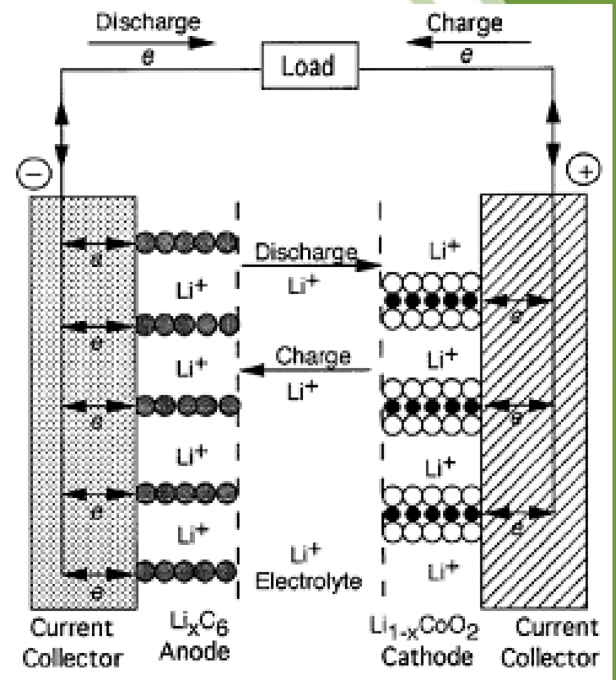


Existing Li Ion Battery Technology

Graphite: 370 mAh/g (Anode)

$LiCoO_2$: 274 mAh/g (Cathode)

→ The energy density can not meet the application needs.

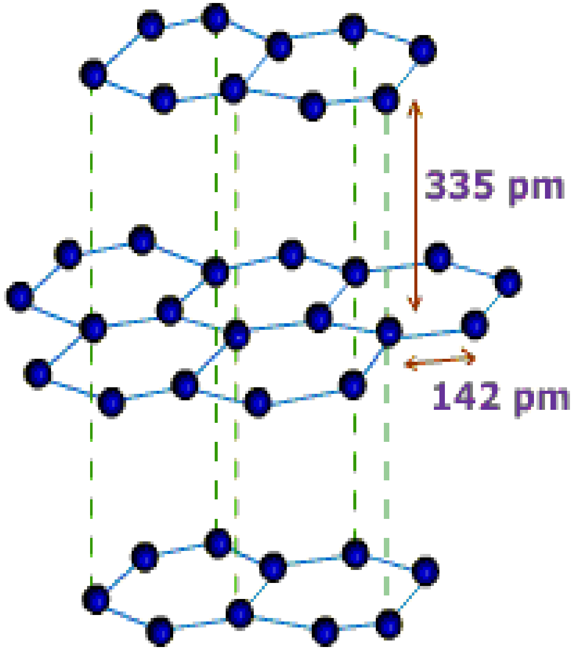


1. Energy density: - Anode and cathode Li storage capacity
   - Voltage
2. Power density: - Li ion moving rate
   - Electron transport
3. Cycle, calendar life and safety: strain relaxation and chemical stability.
4. Cost: Abundant and cheap materials

Graphite- 370 mA.h/g

- Graphite is commonly selected anode material in LIB

- However, the specific capacity of graphite is relatively low since every six carbon atoms can host only one lithium ion by forming an intercalation compound (LiC_6).

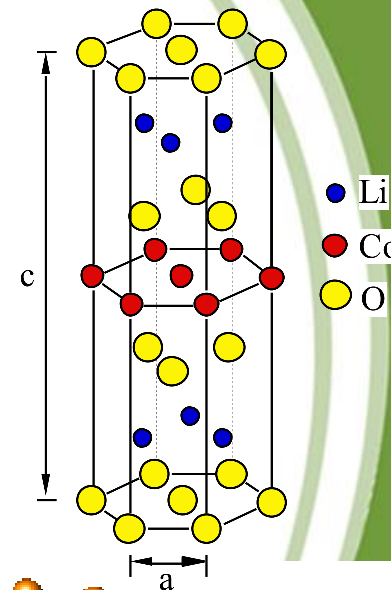


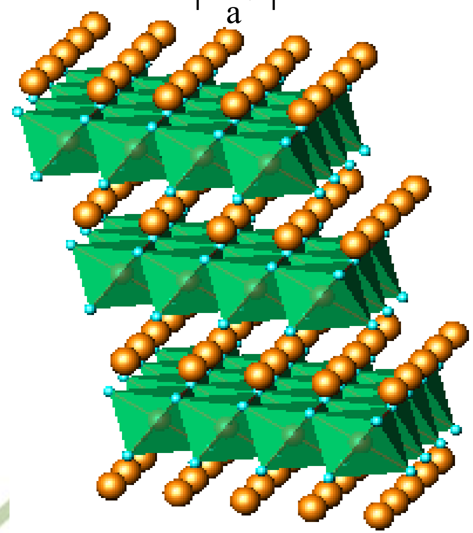
- Sn: 993 mA.h/g, Si: 4200 mA.h/g via the formation of alloys with lithium or through the reversible reactions with lithium ions.

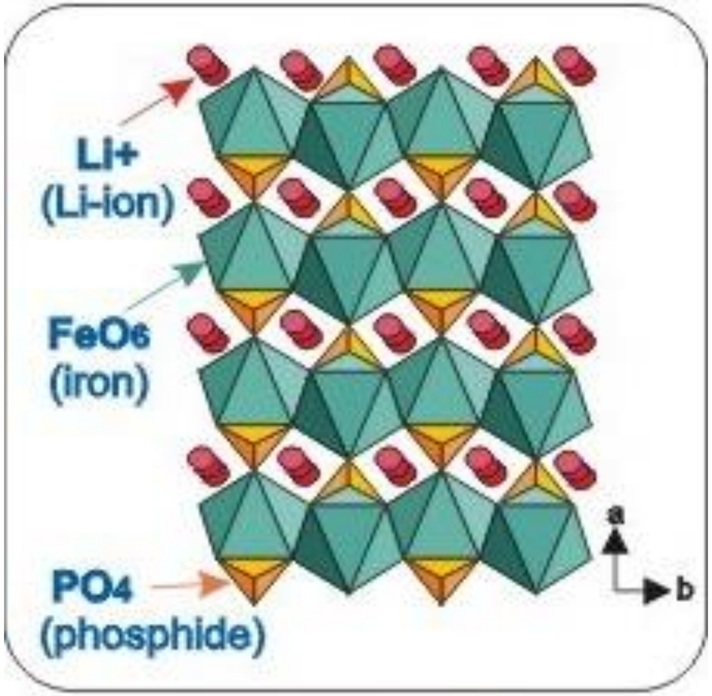
- Drawback: huge volume variation →poor reversibility.

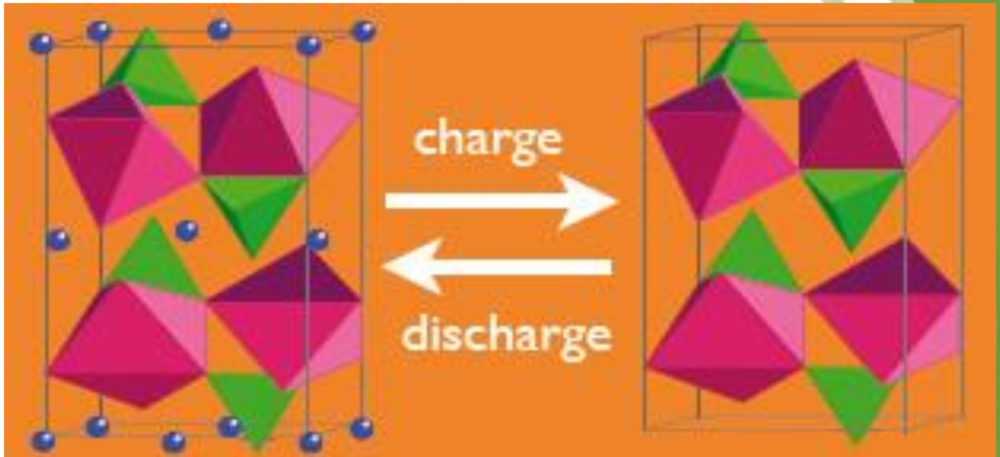
LiCoO2- 274 mA.h/g

- $LiCoO_2$ is the most widely used positive electrode.
- Capacity is limited to almost half the theoretical value due to a hexagonal to monoclinic phase transformation upon charging between 4.15 and 4.2V.
- The dissolution of cobalt ions (Co4+) has also been reported as a reason for the deterioration of the crystal structure.
- Various metal oxides (e.g.,MgO,Al_2O_3, ZnO) and metal phosphates (e.g., $AlPO_4$, $FePO_4$) have been coated on the surface of $LiCoO_2$ substitution of metal elements for Co in $LiCoO_2$ → improve the cyclability of $LiCoO_2$.









The olivine structure is stable during Li-ions insertion and extraction.

Cathode	*Electric Conductivity*	*Solid diffusion coefficient*
$LiCoO_2$	10^{-3}~10^{-4} S/cm	10^{-7}~10^{-9} cm^2/s
$LiMn_2O_4$	10^{-5}~10^{-6} S/cm	10^{-9}~10^{-12} cm^2/s
$LiFePO_4$	10^{-9}~10^{-10} S/cm	10^{-12}~10^{-14} cm^2/s

Comparison data among various Lithium base batteries

Battery	$LiFePO_4$	$LiCoO_2$	$LiMn_2O_4$	$Li(NiCo)O_2$
Stability	Stable	Not Stable	Acceptable	Not Stable
Environmental Concern	Most Enviro-friendly	Very Dangerous		Very Dangerous
Cycle Life	Best/ Excellent	Acceptable	Acceptable	Acceptable
Power/Weight Density	Acceptable	Good	Acceptable	Best
Long Term Cost	Most Economic/ Excellent	High	Acceptable	High
Temperature Range	Excellent (-20 to 70°C)	Decay Beyond (-20 to 55°C)	Decay Extremely Fast over 50° C	-20 to 55°C

Comparison data among various Lithium base batteries

Material	Capacity in theory	Real capacity	Density	Character
$LiCoO_2$	275	130-140	5.00	Stable, high capacity ratio, smooth discharge platform, low life cycle
$LiNiO_2$	274	170-180	4.78	Very high capacity, poor stability, low material cost
$LiMnO_4$	148	100-120	4.28	Low material cost, better in safety, poor high temperature performance, Poor charge/discharge character
$LiFePO_4$	170	120-160	3.25	Low material cost, better in safety, very long cycle life, poor conductivity

Thanks for your attention !