Flexible batteries for wearable devices

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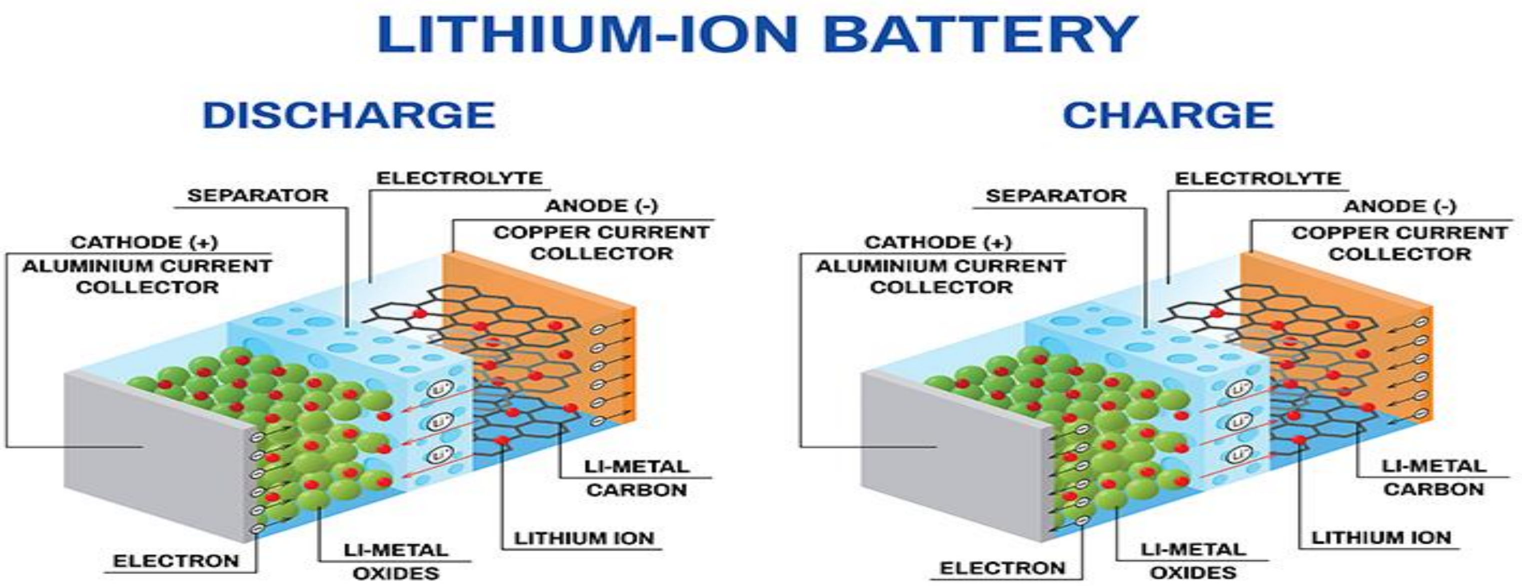
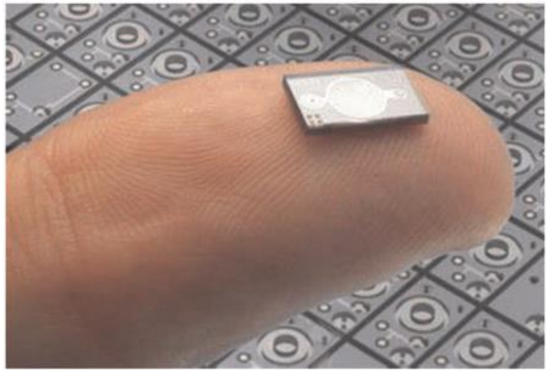
Batteries: General Concept

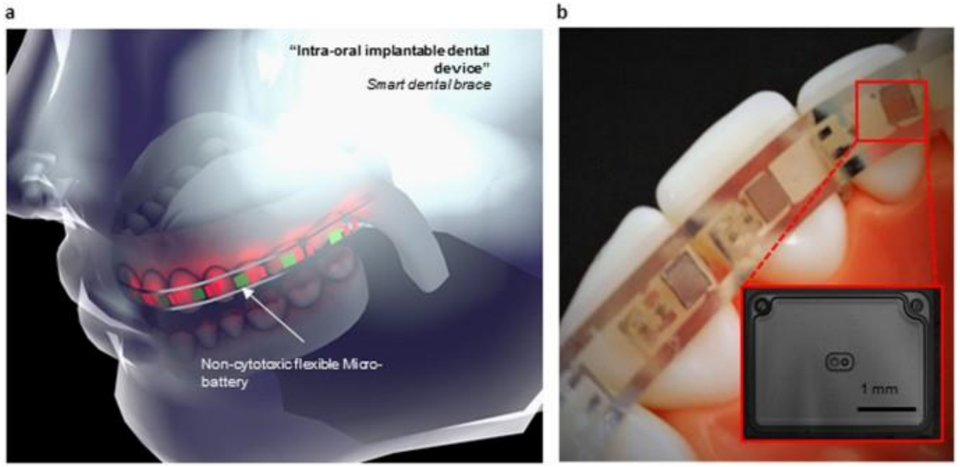
- Current Collectors: Al, Cu
- Electrodes: Metal oxides(positive terminal), Carbon(neg terminal)
- Active material: Li_2O
- Electrolyte: Lithium based gel or polymer
- Separators: Polyethylene, Polypropylene



Flexible batteries: Need

- Internet of things
- Foldable displays
- Wearable and Implantable devices
- RFID tags



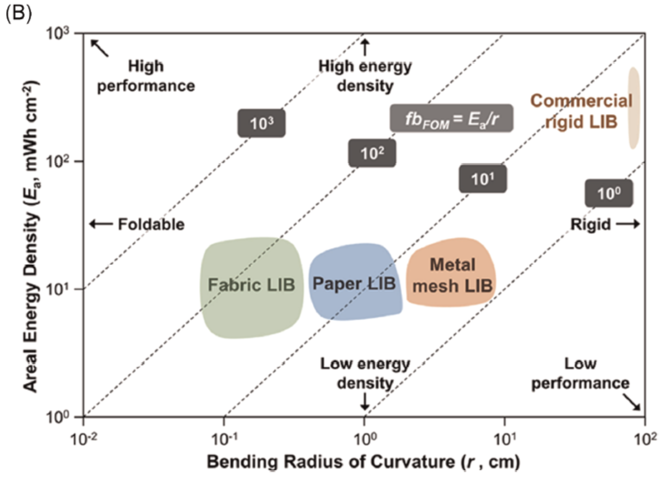


Flexible batteries: Desired Properties

High energy density, high flexibility, and dynamically stable power output should be achieved simultaneously in flexible batteries.

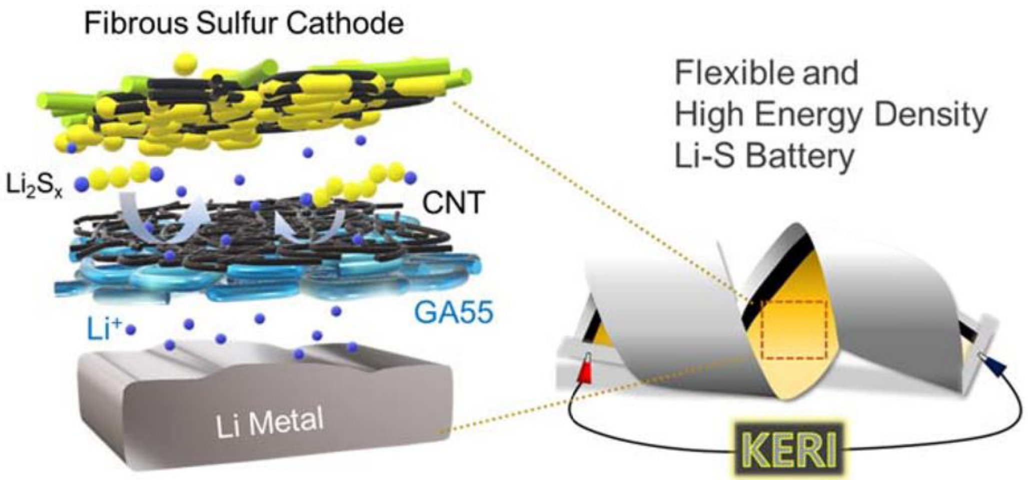
Mechanical properties: For flexible electronics minimum strain should be 5%.(by institute of printed electronics)
Energy Density: Energy density relates to the amount of energy that can be stored per battery unit. Standard Li-ion batteries have ED around 100-270Wh/kg.
Flexible batteries figure of merit(*fbom*): Volumetric energy density* strain.

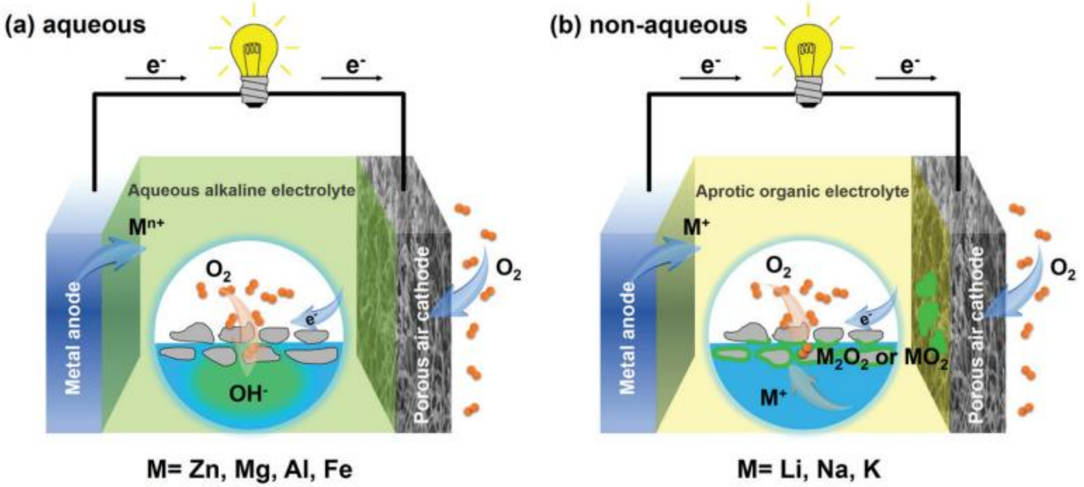
fbFoM = Ea/r.
Ea = aerial energy density
R = bending radius



Technologies

- Metal gas
  - Metal-CO_2
  - Metal O_2
- Li ion
- Li-S
- Polymer based batteries

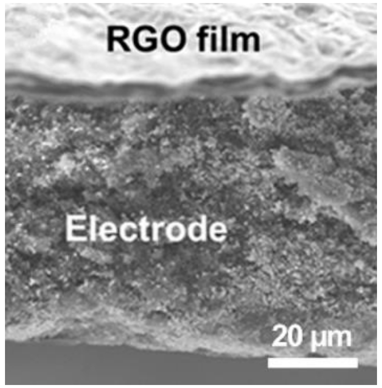


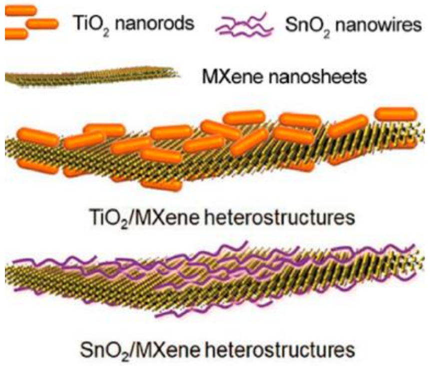


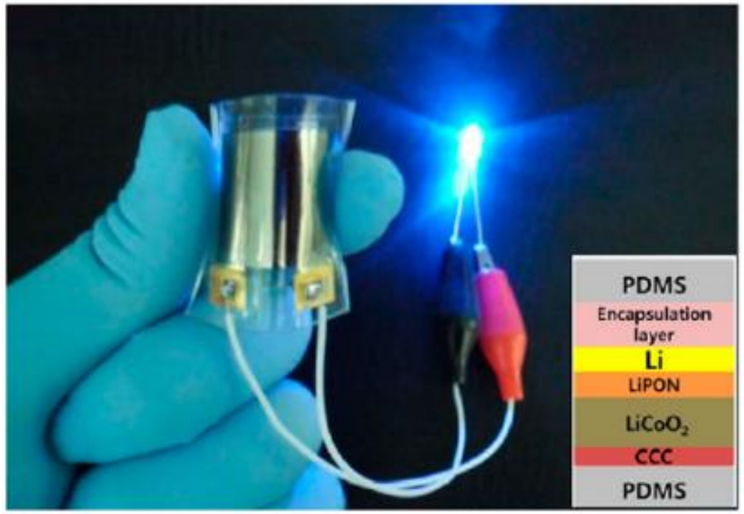
Li-Ion Batteries

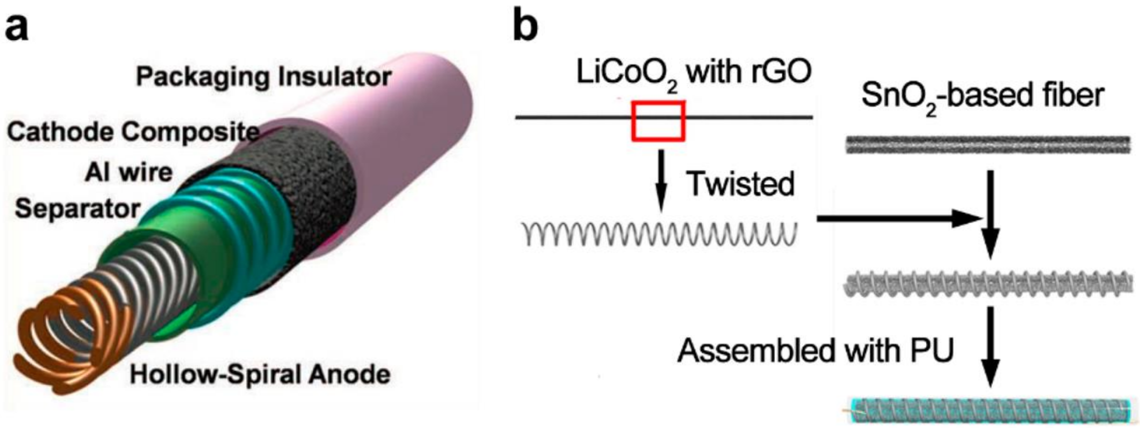
How to make them flexible?

1. Using porous materials.
2. Superslim batteries
3. Structural & topological changes





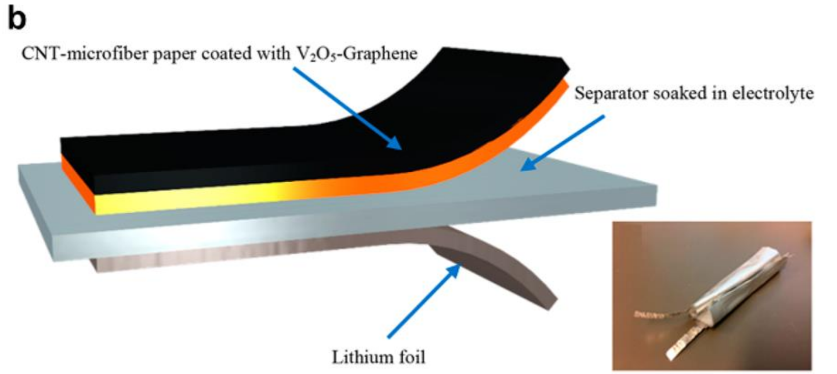




Porous Materials: Current collectors

Standard materials used: Al and Cu.

- Materials:
  1. **Al and Cu:** Can be made flexible but not used because of low yield strain(0.9 and 1.2% respectively).
  2. **Carbonaceous and Polymers**: CNTs, Carbon Fibers, carbon cloth (CC),graphene,polyacrylonitrile (PAN), cellulose. High flexibility, extraordinary conductivity, light-weight and large surface area.
  3. **RGO:** (in 2016), Highly porous, conductive film (>3112 S/cm). fabricated by a solution based filtration process followed by thermal reduction (773 K), and then a high temperature reduction (2750 K by Joule heating)



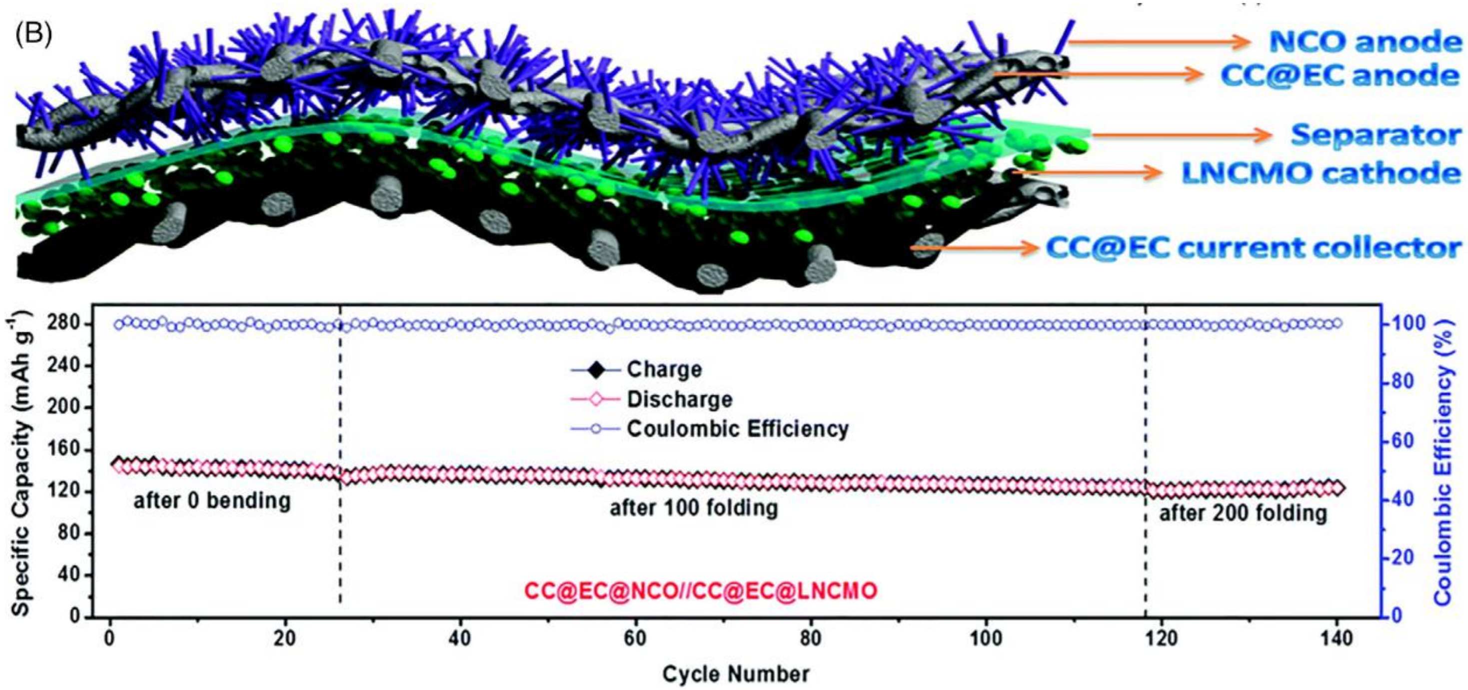
Fabricated by depositing single-wall CNTs over wood microfibers through a layer-by-layer self-assembly process.

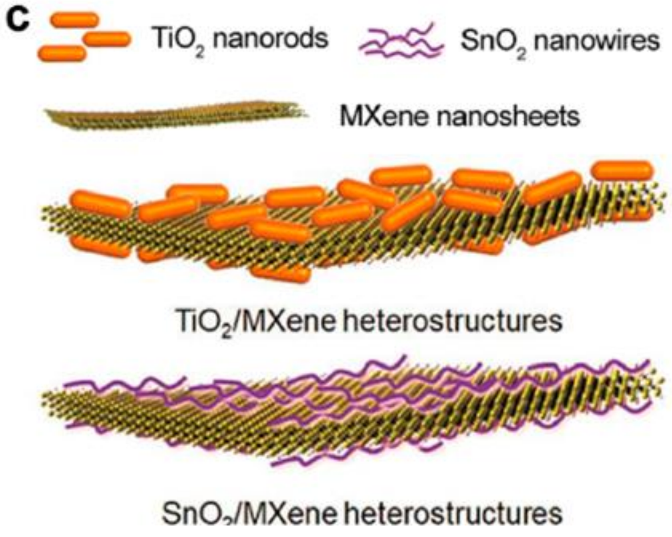
Porous Materials: Electrodes

Standard materials used: Metal oxides and Carbon based

- Materials:
  1. The electrodes are usually fabricated/ selected in a way, that it can interact well with the current collectors. This helps to increase the adhesion stress and area. For eg. the composite cathode of the poly-compound (PDHBQS) interlocked with single-wall carbon nanotubes (SWCNTs) has been fabricated for flexible LIBs. (discharge capacity of 182 mAh/g at 50 mA/g).
  2. **TiO_2 nanorods and SnO_2 nanowires on MXene nanaosheets** as porous anode for Li-ion batteries.
  3. C Cloth with exfoliated porous Carbon shell(CC@EC) as CC. $NiCo_2O_4$ anode and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode are grown over CC@EC. Excellent properties of capacity retention after multiple bending cycles.
  4. Some other porous materials include: **Li Titanium oxide grown on Ti foil**, porous **$LiCoO_2$** nanosheet array and porous **$LiMn_2O_4$** nanosheets
     The electrodes can be printed using common printing techniques: 3D, Aerosol gel, inkjet and stencil.

Porous Materials: Electrodes





FLIB with $NiCo_2O_4$ anode and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode on carbon cloth current collectors.

The monolithic CC@EC@NCO CDS architectures are fabricated by the thermal reduction and etching of the hydrothermally produced $Ni(OH)_2 \cdot H_2O$ nanosheets

Porous Materials: Electrolytes

Standard materials used: Li based gels or polymers
Considerations: Solid vs Liquid electrolytes. Liq elec. Usually not used in flexible Li-ion batteries.

Materials:

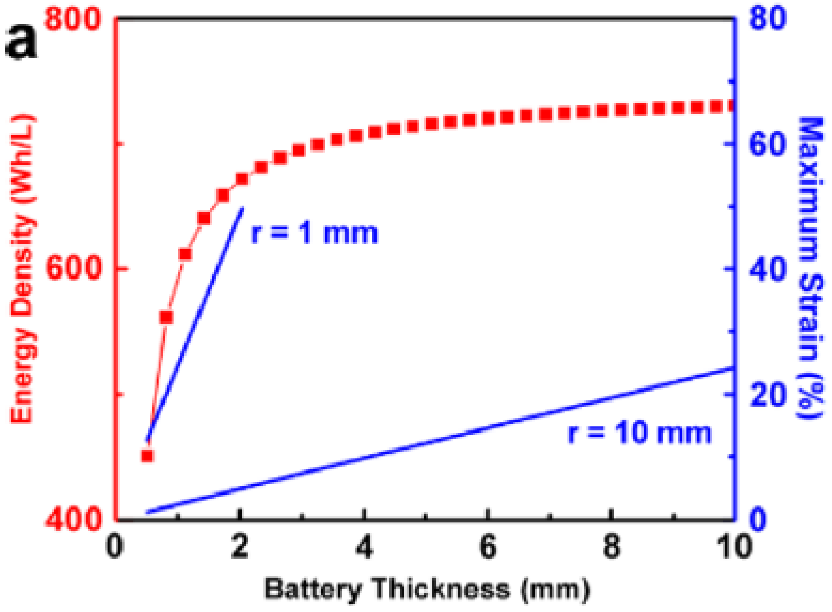
1. GPEs(Gel Polymer electrolyte): Polyethylene oxide, Polyimide, poly(ethylcyanoacrylate), poly(vinylidene fluoride) (PVDF), poly(arylene ether),and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)

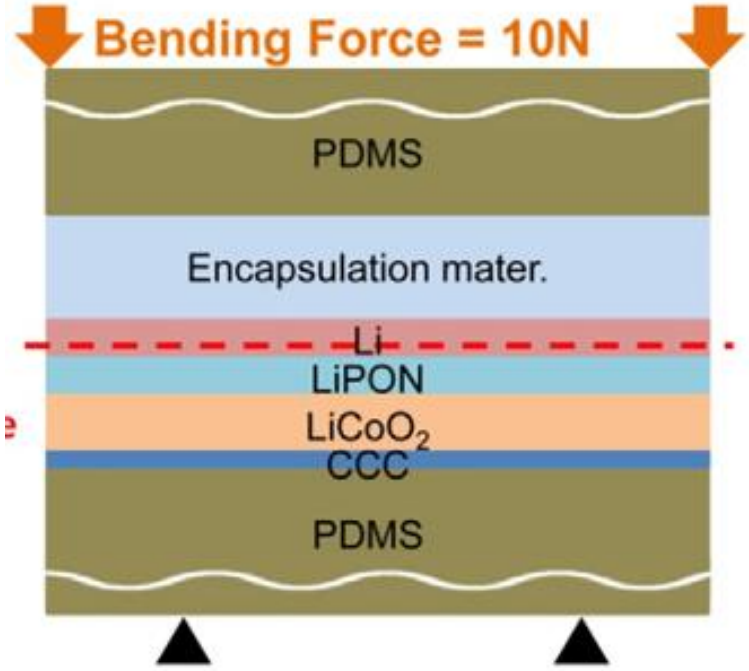
1. SPEs(Solid-state polymer electrolytes): LLZO($Li_7La_3Zr_2O_{12}$) and PEO based solid electrolyte : high ionic conductivity and flexibility, flexible CSE with vertically aligned columns of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP): good ionic conductivity and flexibility. Many other complex compounds can be used as an electrolyte while maintaining flexibility and good ionic conductivity.

Superslim batteries

Technology: Thinning. Thin materials are used to make the batteries.

Strain = t/2r



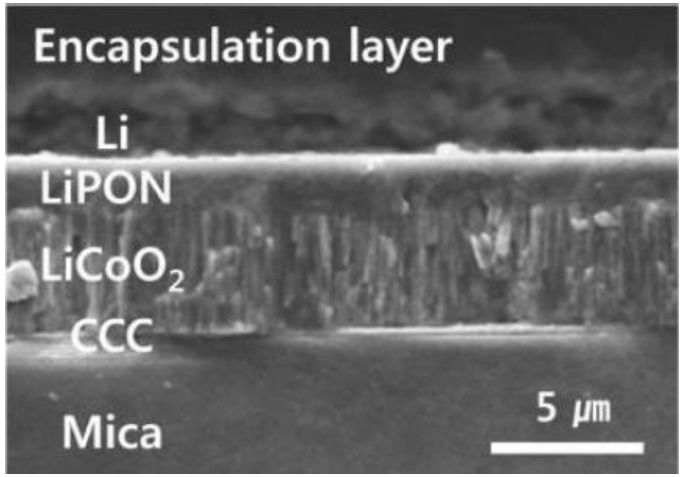


Superslim batteries: Materials

Substrate : PDMS/ Mica
Electrodes

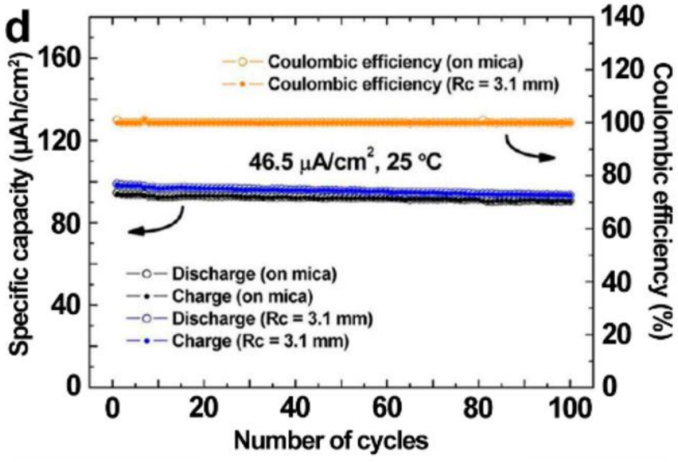
- Anode: Li metal
- Cathode: Lithium cobalt oxide

Electrolyte: Lithium phosphorus oxynitride(LiPON)
Current collectors: Cathode current collector(CCC)



The same battery is also being manufactured with PDMS Substrate on both the sides.
Some properties:

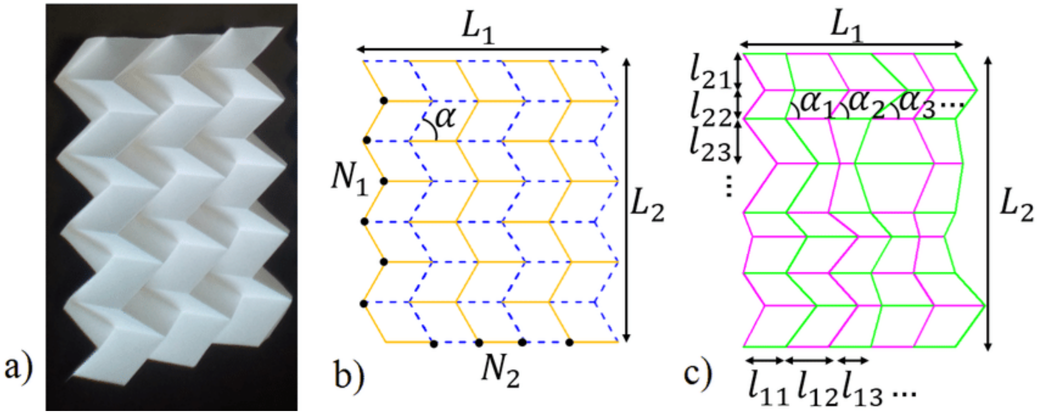
- Capacity = 106 uAh/cm2
- Capacity retention = 94.5% after 100 cycles

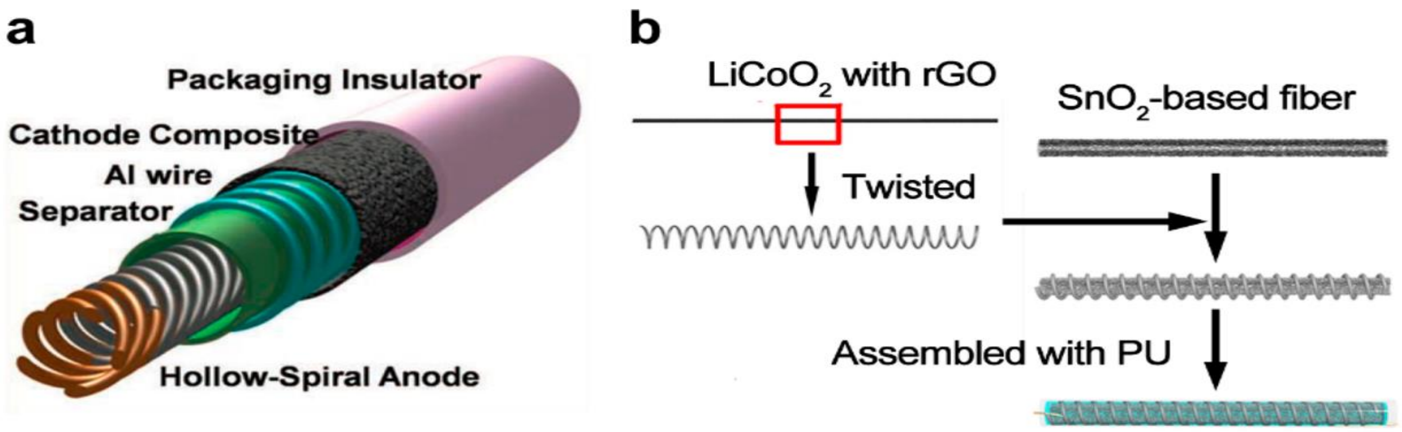


Topological batteries

Flexible batteries can also be realized by optimizing the structure of the cells. Some of these structures include:

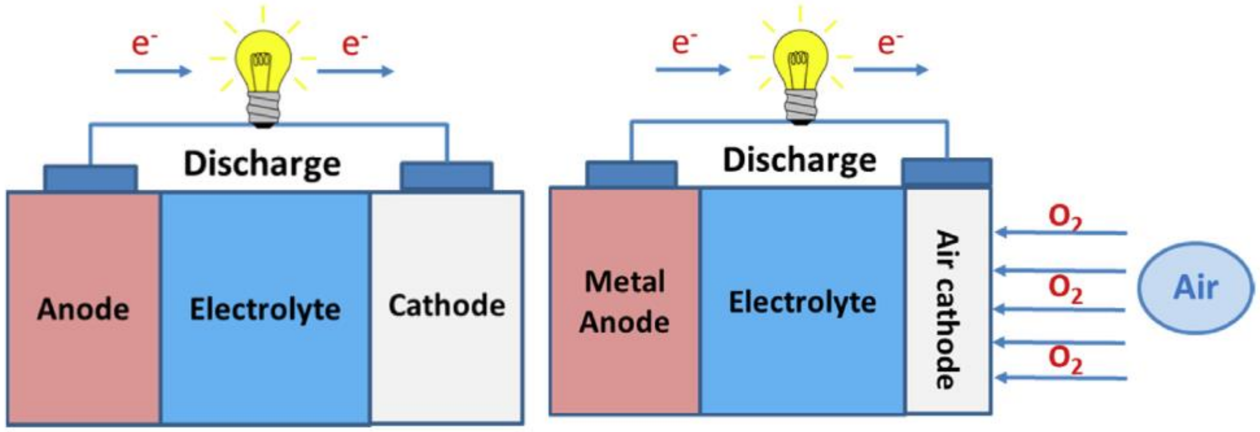
- Wire-shaped
- cable-type
- Wave-like
- miura pattern





Metal Gas Batteries

- The basic working principle of the battery relies on the chemical reaction between metal ions and gases available in the air such as O_2 and CO_2.
- Significant advantages:
  - Excellent energy storage capacity
  - Reversibility of reaction
  - Sufficient service life
- Challenges faced:
  - Sluggish reaction rates
  - Catalysis decay
  - Difficult quick charging
- Structure



(a) Standard battery structure (b) MAB structure

Metal-O_2 Batteries

Governing discharge equation (Aqueous):

Anode:

$$M \rightleftharpoons M^{+} + e^{-}$$

Cathode:

$$O_2 + 2H_2O + ne^{-} \rightleftharpoons 4OH^{-}$$

Governing discharge equation (Non-Aqueous):

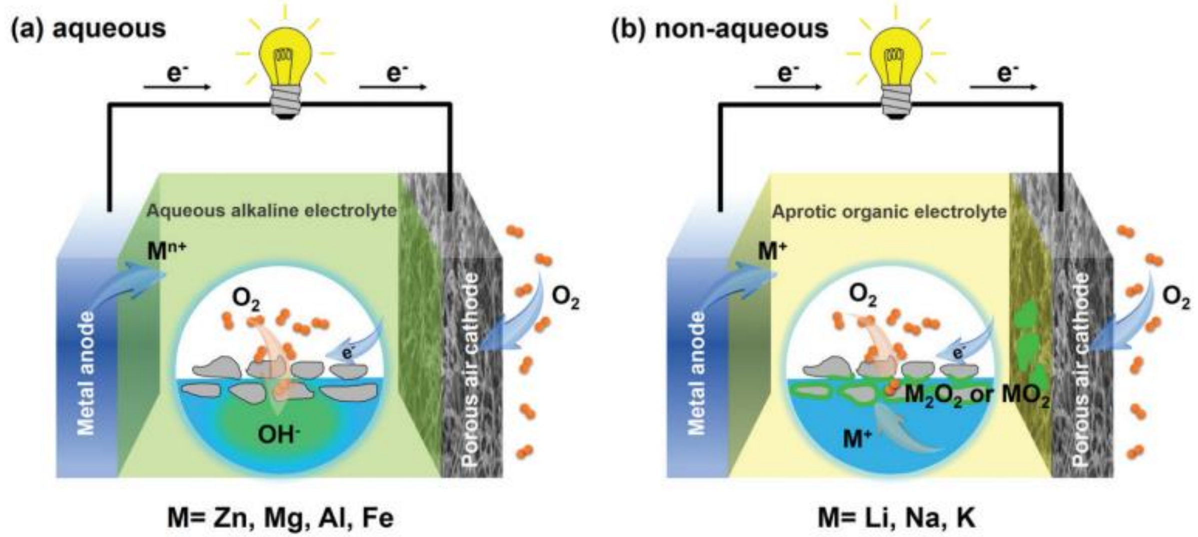
Anode:

$$M \rightleftharpoons M^{+} + e^{-}$$

Cathode:

$$mM + O_2 + me^{-} \rightleftharpoons M_mO_2 \quad (m = 1 \text{ or } 2)$$

Examples: Zinc-Air Batteries (ZAB), Li-O_2 Batteries



Metal-O_2 Batteries: Flexible ZAB

Governing Equation:

Cathode:

$$O_2 + 4H_2O + 4e^- \rightleftharpoons 4OH^-$$

Anode:

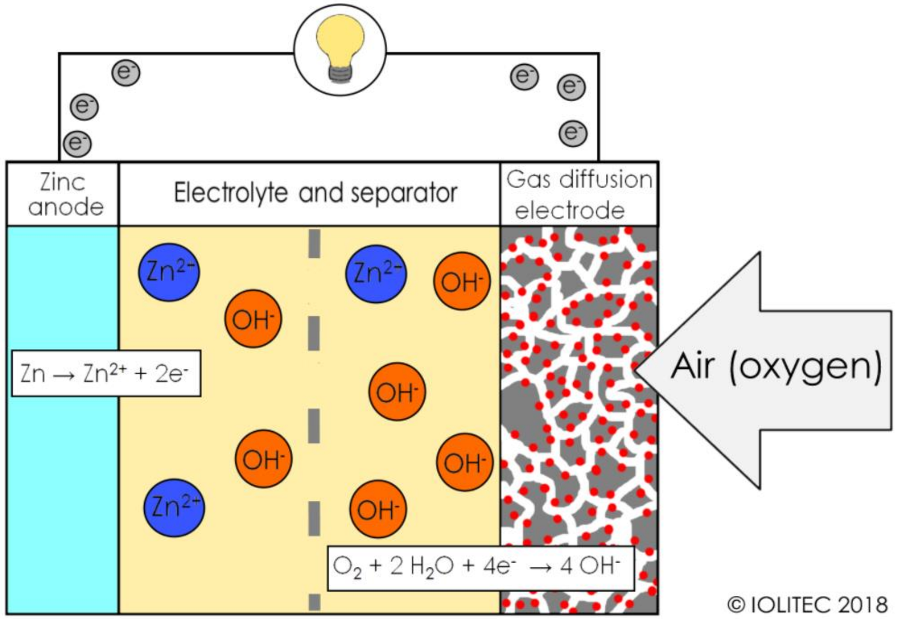
$$Zn + 4OH^- \rightleftharpoons Zn(OH)_4{}^{2-} + 2e^-$$

$$Zn(OH)_4{}^{2-} \rightleftharpoons ZnO + H_2O + 2OH^-$$

Overall:

$$2Zn + O_2 \rightleftharpoons 2ZnO \quad (E^\theta = 1.65\ V)$$

- Only commercialized metal-gas battery → hearing aids
- Energy density (theoretical) = 1084 W h kg-1
- Equilibrium potential = 1.65 V



Metal-O_2 Batteries: Flexible ZAB

Flexible Air Cathodes:

1. *Spraying Technique:* Catalyst sprayed onto porous current collector
   a. N-doped CNT/reduced graphene oxide (rGO) hybrid
   b. Cross-stacked aligned CNT sheets dipped in RuO2 catalyst ink
   c. Co atoms dispersed in coordination polymers
2. *In-Situ Construction:* Integration of catalyst and/or a current collector into free standing electrodes
   a. Flexible carbon cloth with oxygen abundant functional groups (acid oxidation, air calcination)
   b. Graphene hydrogel or B-doped graphene quantum dots (self assembly of rGO during hydrothermal process)

Flexible Zn Anodes:

- Materials such as Zn foils or Zn wires used
  - Lower cost, simplified process
  - Good mech strength, flexibility, easy processing
  - Other options excessive (in terms of Zn quantity)
- Challenges:
  - Low utilization of anode → low energy density
  - Pure Zn easily damaged (inherent metal fatigue)
  - Dendritic crystals → damage cell
- Solutions derived from ZIBs:
  - Epitaxial deposition of Zn with proper crystal orientation
  - ZnF_2 rich SEI film on Zn anode (stable cycling performance)
  - Zn/CNT/CNF anodes (dendrite reduction)

Metal-CO_2 Batteries

- Promising candidate for next generation batteries
  - High energy density
  - CO_2 capture
- Li-CO_2, K-CO_2, Na-CO_2, Al-CO_2, Zn-CO_2
- Li-CO_2 most promising
  - Working Voltage → 2.8 V
  - Energy Density → 1875 W h kg -1

Table 4 Theoretical voltage, capacity, energy density, and chemical reaction mechanism of other categories of metal–CO_2 batteries known to date

Battery type	Chemical reaction mechanism (electrolyte categories)	Cathode catalyst	Theoretical voltage (V)	Theoretical capacity (mA h g^{-1})	Theoretical energy density (W h kg^{-1})
Li–CO_2[189]	$4Li + 3CO_2 \rightleftharpoons 2Li_2CO_3 + C$ (organic LiTFSI/TEGDME)	CNT/graphene	2.80	670	1876
Na–CO_2[191]	$4Na + 3CO_2 \rightleftharpoons 2Na_2CO_3 + C$ (organic $NaClO_4$/TEGDME)	Activated MCNT	2.35	480	1130
K–CO_2[190]	$4K + 3CO_2 \rightleftharpoons 2K_2CO_3 + C$ (organic KTFSI/TEGDME)	N-CNT–rGO	2.48	372	922
Al–CO_2[30]	$4Al + 9CO_2 \rightleftharpoons 2Al_2(CO_3)_3 + 3C$ (ionic liquid $AlCl_3$/[EMIm]Cl)	Au@Pd	~0.72	638	~460
Zn–CO_2 (1)[24]	$Zn + CO_2 + H_2O \rightleftharpoons ZnO + HCOOH$ (aqueous KOH/NaCl)	3D Pd nano-sheets	0.955	825 420	788 (Zn) 402 (ZnO + HCOOH)
Zn–CO_2 (2)[44]	$Zn + CO_2 + H_2O + 2OH^- \Rightarrow Zn(OH)_4^{2} + CO$ (discharge) $Zn(OH)_4^{2-} \Rightarrow Zn + 1/2O_2 + 2OH^- + H_2O$ (charge) (aqueous KOH/$KHCO_3$)	Ir@Au	0.707	825 332	583 (Zn) 235 ($Zn(OH)_4^{2-}$ + CO)

Metal-CO_2 Batteries: Li-CO_2

Cathode:

$$2CO_2 + 2e^- \rightarrow C_2O_4^{2-}$$

$$C_2O_4^{2-} \rightarrow CO_2^{2-} + 2CO_2$$

$$CO_2^{2-} + C_2O_4^{2-} \rightarrow 2CO_3^{2-} + C$$

$$2Li^+ + CO_3^{2-} \rightarrow 2Li_2CO_3$$

Anode:

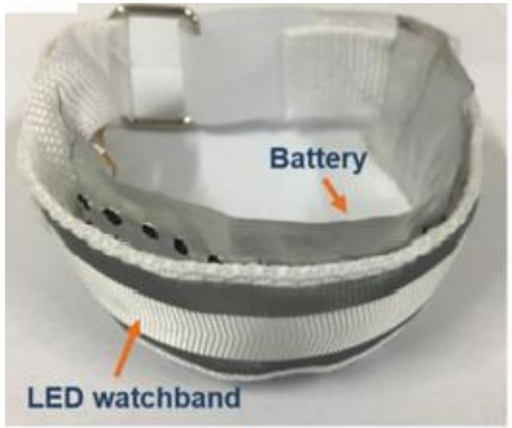
$$Li \rightarrow Li^+ + e^-$$

Overall:

$$4Li + 3CO_2 \leftrightarrow 2Li_2CO_3 + C \quad (E^0 = 2.80\ V)$$

Flexible Air Cathodes:

- *For Planar Batteries:*
  - N-doped carbon with MoFeNi and MoC nanocomposites on nickel foam
  - Ru/C-based cathode
  - Ir/C nanofiber networks
- *For Fiber Shaped Batteries:*
  - N-doped CNTs networks anchored on Ti wires
  - Mo2C nanoparticles on CNT cloth hybrid films



Polymer Based Batteries

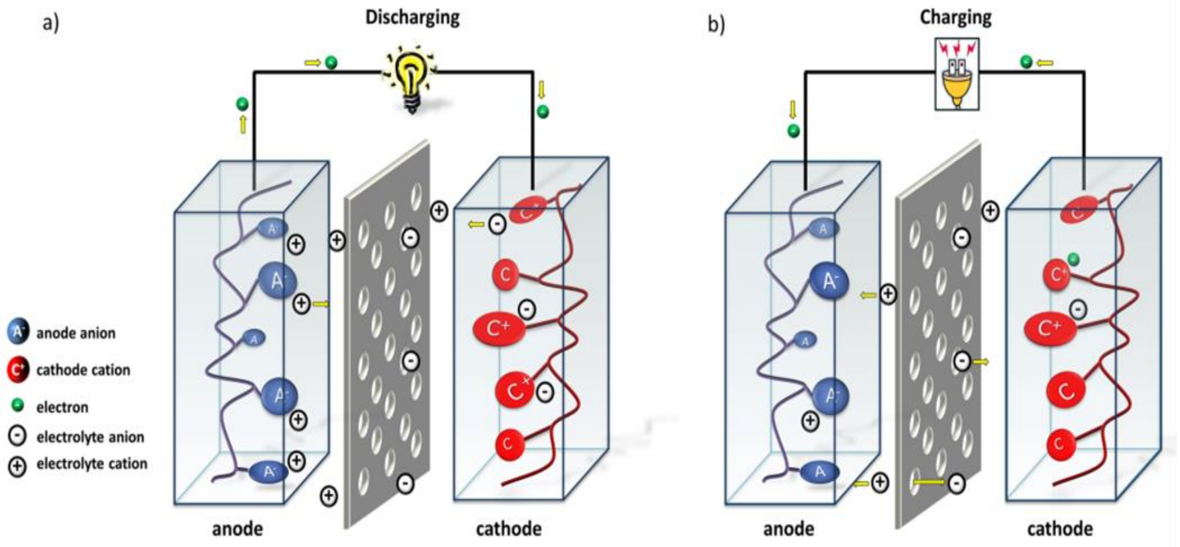
Batteries that use organic redox-active polymers instead of metals for either electrode, cathode or anode are polymer-based batteries.

Advantages over Li-ion batteries -

- Excellent rate performance
- Very long cycle life
- Sustainable and recyclable.

Polymer based batteries typically consist of

- Electrodes
  - Active polymer
  - Conductive additive
  - Polymeric binder
- Electrolyte/separator



Polymer based battery in dual ion-configuration

Active materials

1. **Conjugated Polymers**

Advantages - conductivity can be varied through doping

Disadvantages - i. slopping redox potential

ii. limited achievable level of doping

Examples -

a. Polypyrrole (PPy)
b. Polythiophene (PT)
c. Polyaniline (PANI)
d. Polyacetylene
e. Combination with inorganic redox active compounds

2. **Nonconjugated conventional redox-active polymers**

Advantages - non-conductive backbone therefore charge localized over redox sites

Disadvantages - low conductivity

Examples -

a. Carbonyl Compounds
b. Organosulfur Compounds
c. Carbazole
d. Organometallic ferrocene-based compounds

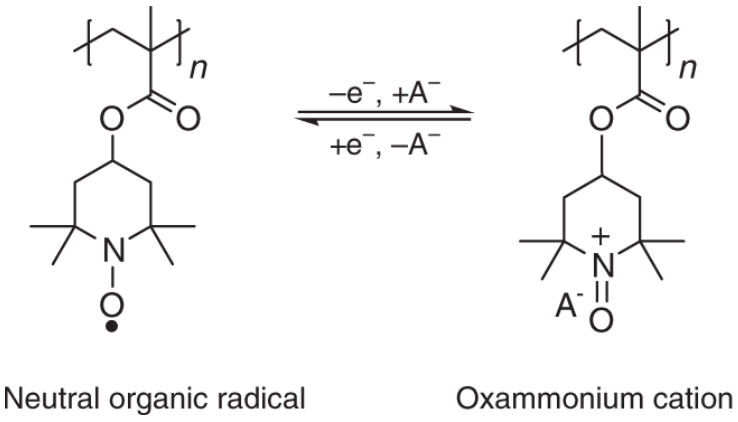
Radical batteries

Organic radical batteries are stable during operation but degradable at end of life.

- **PTMA** (poly(2,2,6,6-tetramethylpiperidinyloxy-4-ylmethacrylate))

PTMA changes into gel like state due to absorption of organic electrolytes and hardly gets damaged when repeatedly gets bent and unbent.
Cross linked PTMA gel has the storage elastic modulus under 10kPa.
PTMA/vapor grown carbon fiber (VGCF) composite show excellent discharge rate properties (20C/1C capacity 91%).

Other examples -
- 2,2,6,6-Tetramethylpiperidinyl-N-oxyl (TEMPO)
- Nitroxide Radicals
- Galvinoxyl

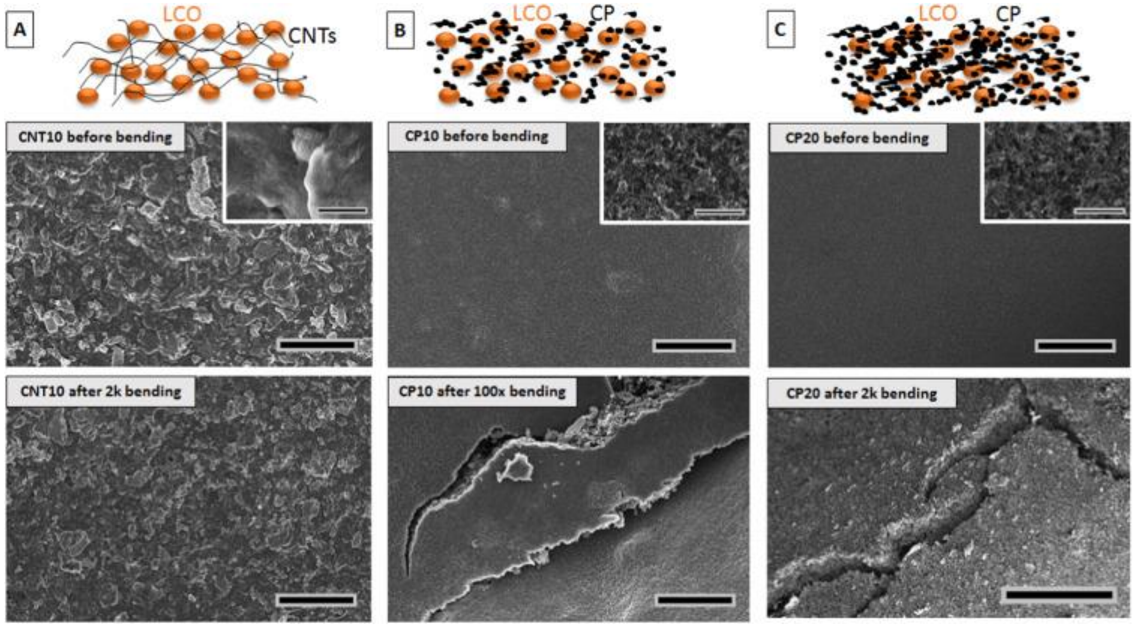


Conductive additive

Non conjugated polymers posses low conductivity therefore additional conductive additives are required.

Example -

- Carbon powder
- Vapor grown carbon fibers
- Graphene or carbon nanotubes
- Graphene or reduced graphene oxide



Work by Sarah et. al. shows that the absence of cracks in the CNT based electrodes suggests that the CNTs form an interconnected network that mechanically binds the active material.

Polymeric binders

Polymeric binders provide mechanical stability and provide good contact between current collector and composite electrodes.
2 to 10 wt % of a composite electrode consists of binders.

Example -

- Carboxymethylcellulose
- fluorinated polymers such as - PVDF(poly(vinylidene difluoride))
  - PTFE (poly(tetrafluoroethylene))

References

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Thank You