FUNCTIONAL POROUS POLYMERS IN ENERGY APPLICATIONS

Clean and Renewable Energy Technologies
Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore
December 1, 2017

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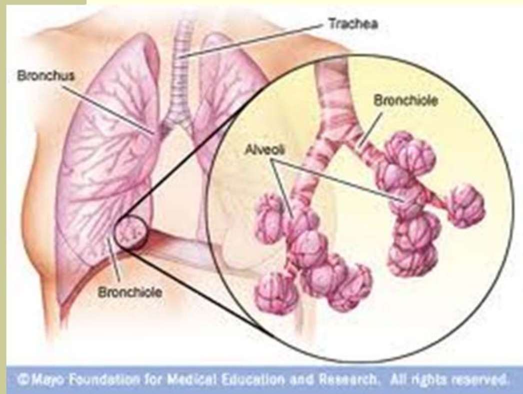
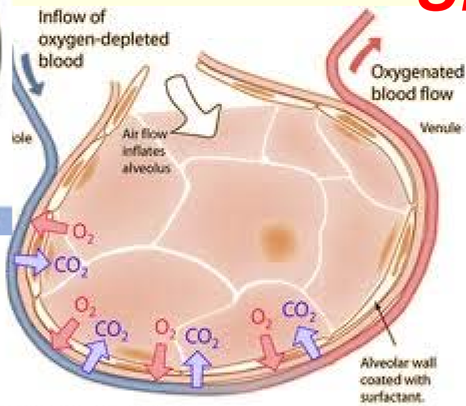
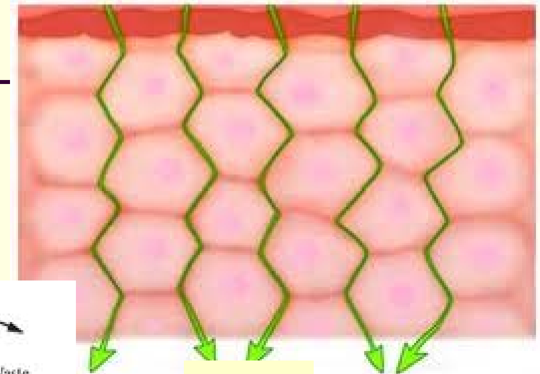
POROUS MATERIALS ARE UBIQUITOUS !

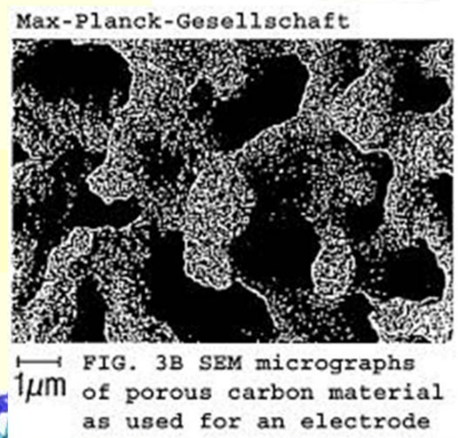




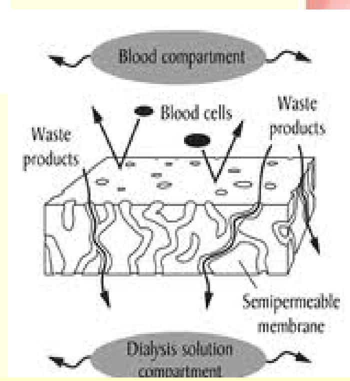
Alveoli in the lungs



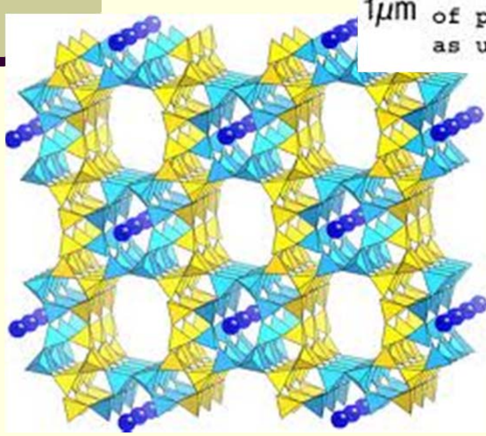
Skin



Porous Carbon electrode

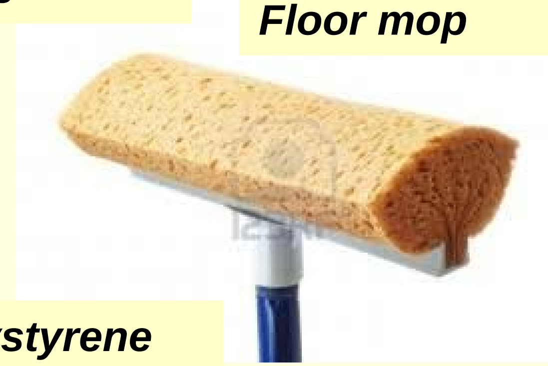


Dialysis Membrane Polyacrylonitrile



Zeolite 4A

Polystyrene foam cup



Polyurethane Floor mop

POROUS POLYMERS

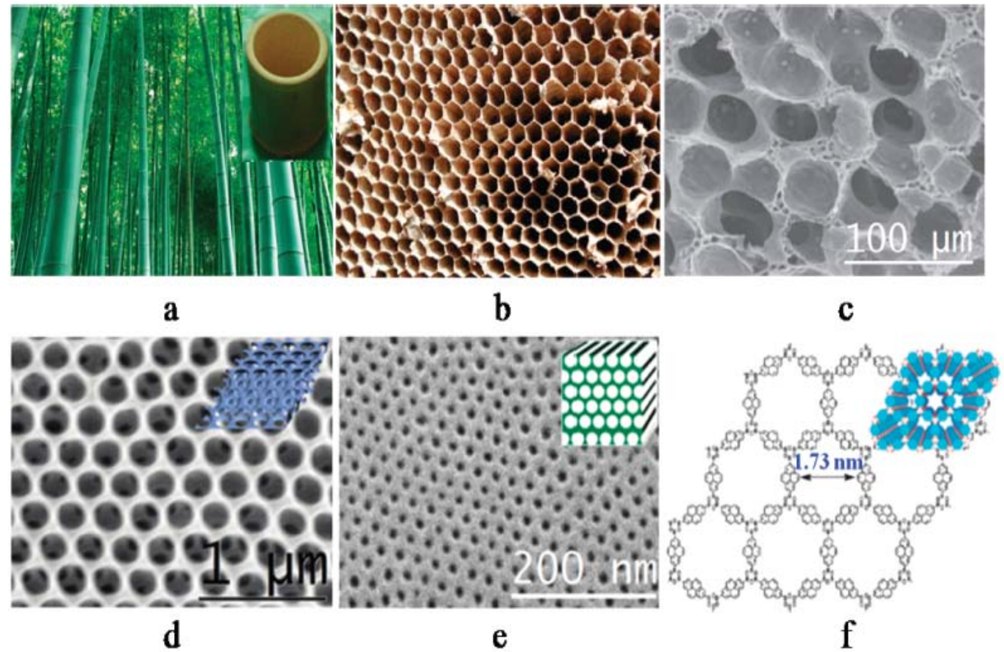
Porous polymers are polymeric materials, which have pores in the structure of polymers. They are classified as :

Microporous < 2 nm.

Mesoporous = 2 to 50 nm.

Macroporous > 50 nm

Qiu, S.; Ben, T. ed. Porous Polymers, RSC, UK, 2015; Wa et al,. Chemical Reviews, 2012; A.G.Slater and A.I.Cooper, Science, 348, 6238, 2015; Zhang et al., J. Mat. Chem.,A 5, 8795, 2017



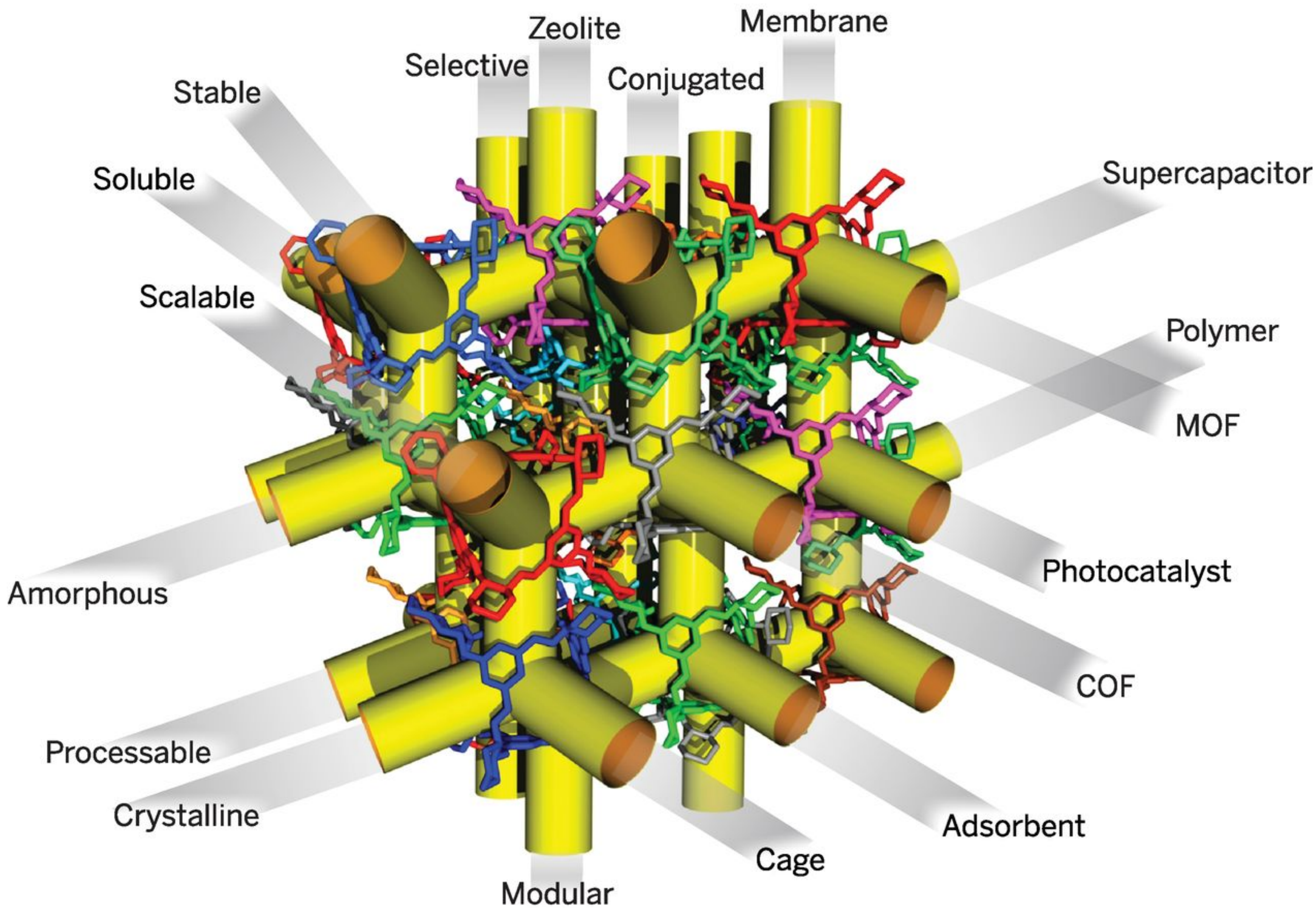
Methods

- Use of hard or soft templates
- Stretching a polymer in the melt or gel state
- Phase inversion methods
- Direct synthesis using appropriately designed monomers
- High internal phase emulsion polymerization

Applications of porous polymers

- o Reverse osmosis membranes
- o Gas storage and separation materials
- o Catalyst supports
- o Tissue engineering and scaffolds
- o **Selective proton and lithium ion transport membranes**

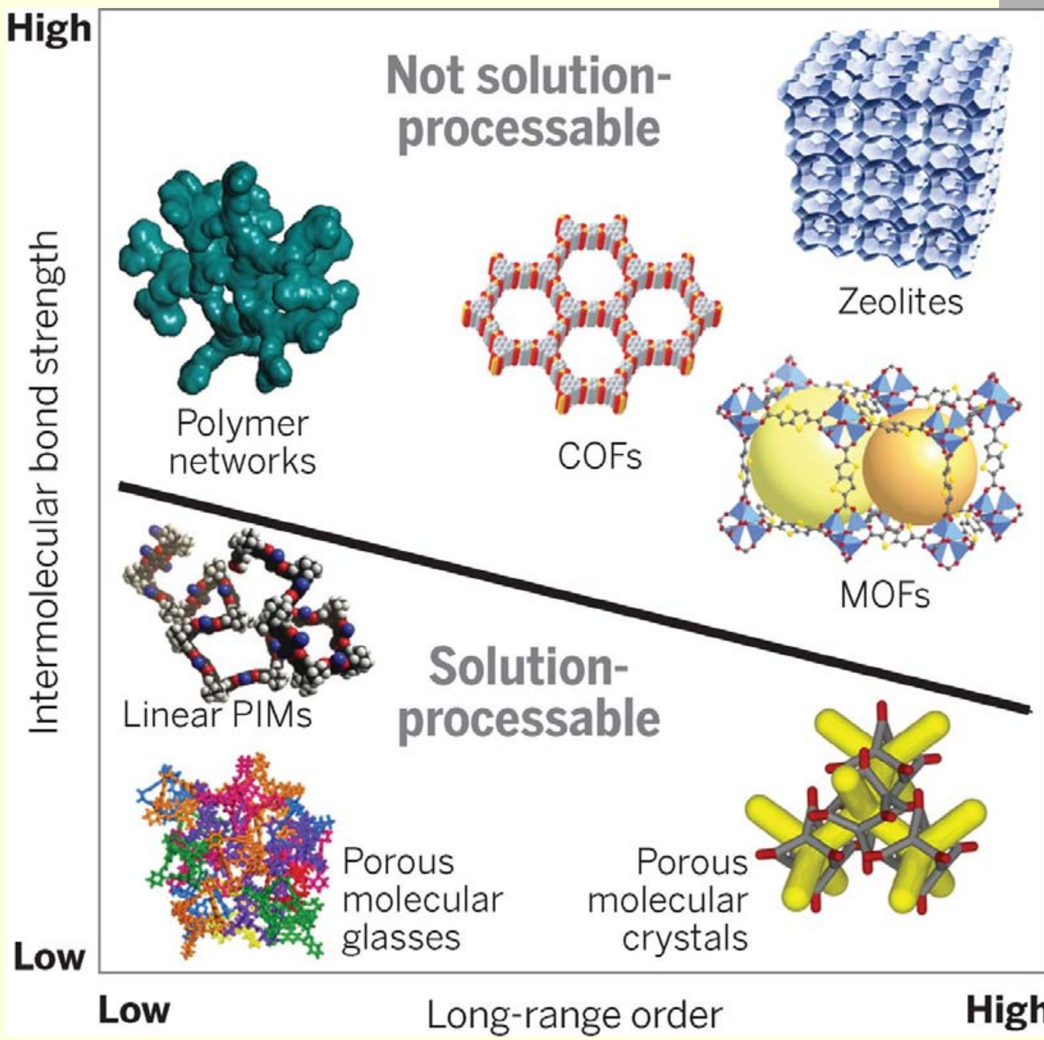
POROUS MATERIALS DEFINED BY TYPE OR BY FUNCTION,



Anna G. Slater, and Andrew I. Cooper, Science 2015, 348, 6238

FUNCTIONAL CLASSIFICATION OF POROUS SOLIDS

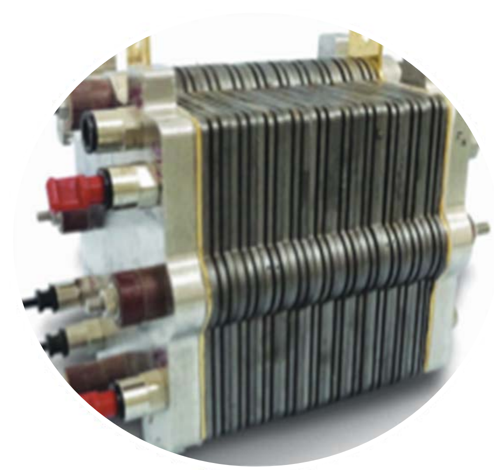
Anna G. Slater, and Andrew I. Cooper Science 2015;348: 6238



FUNCTIONAL POROUS POLYMERS IN ENERGY APPLICATIONS

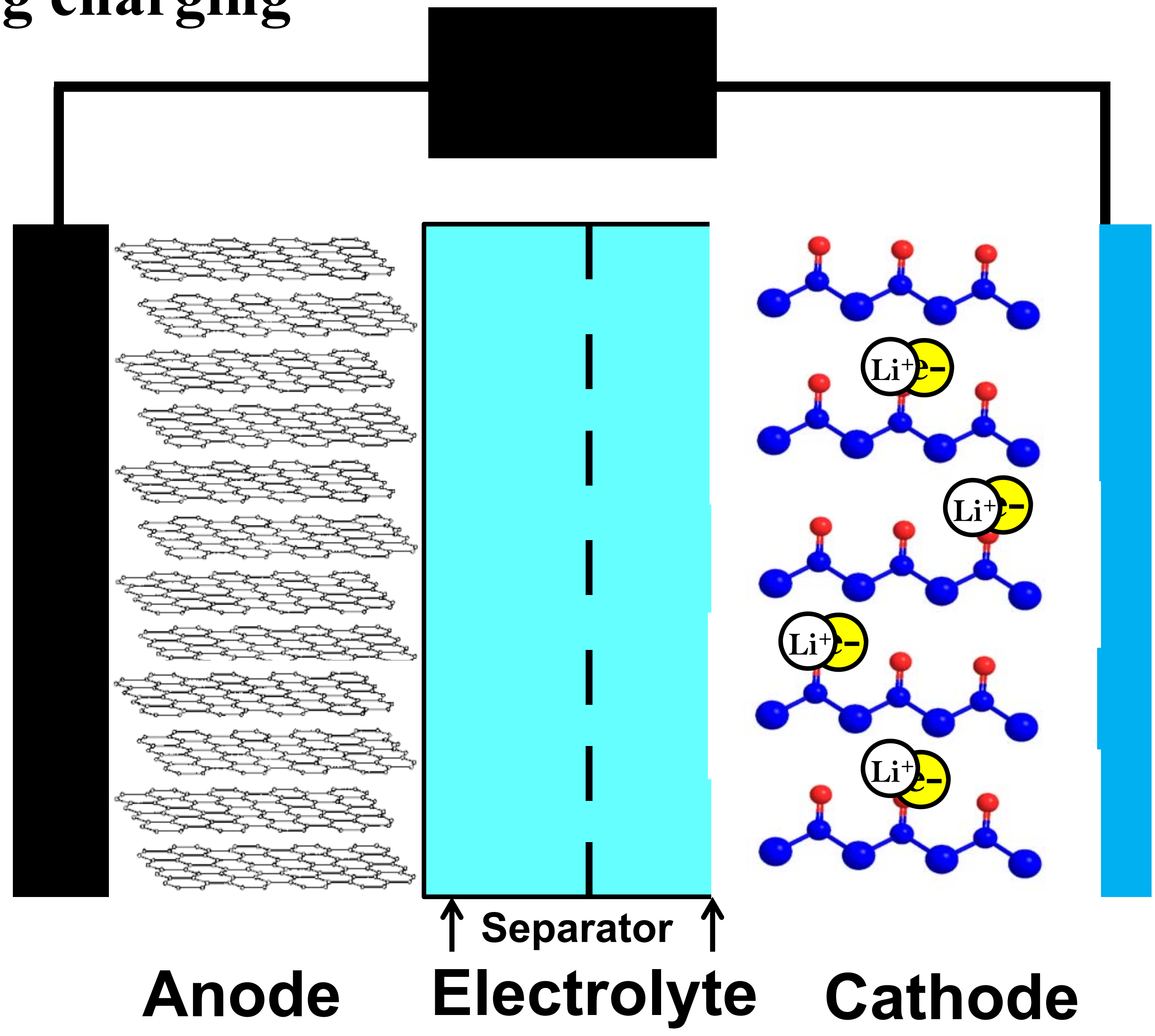
- Energy Storage : Separator membranes for selective lithium ion transport

- Energy Generation : Proton conducting membranes for polymer electrolyte fuel cells



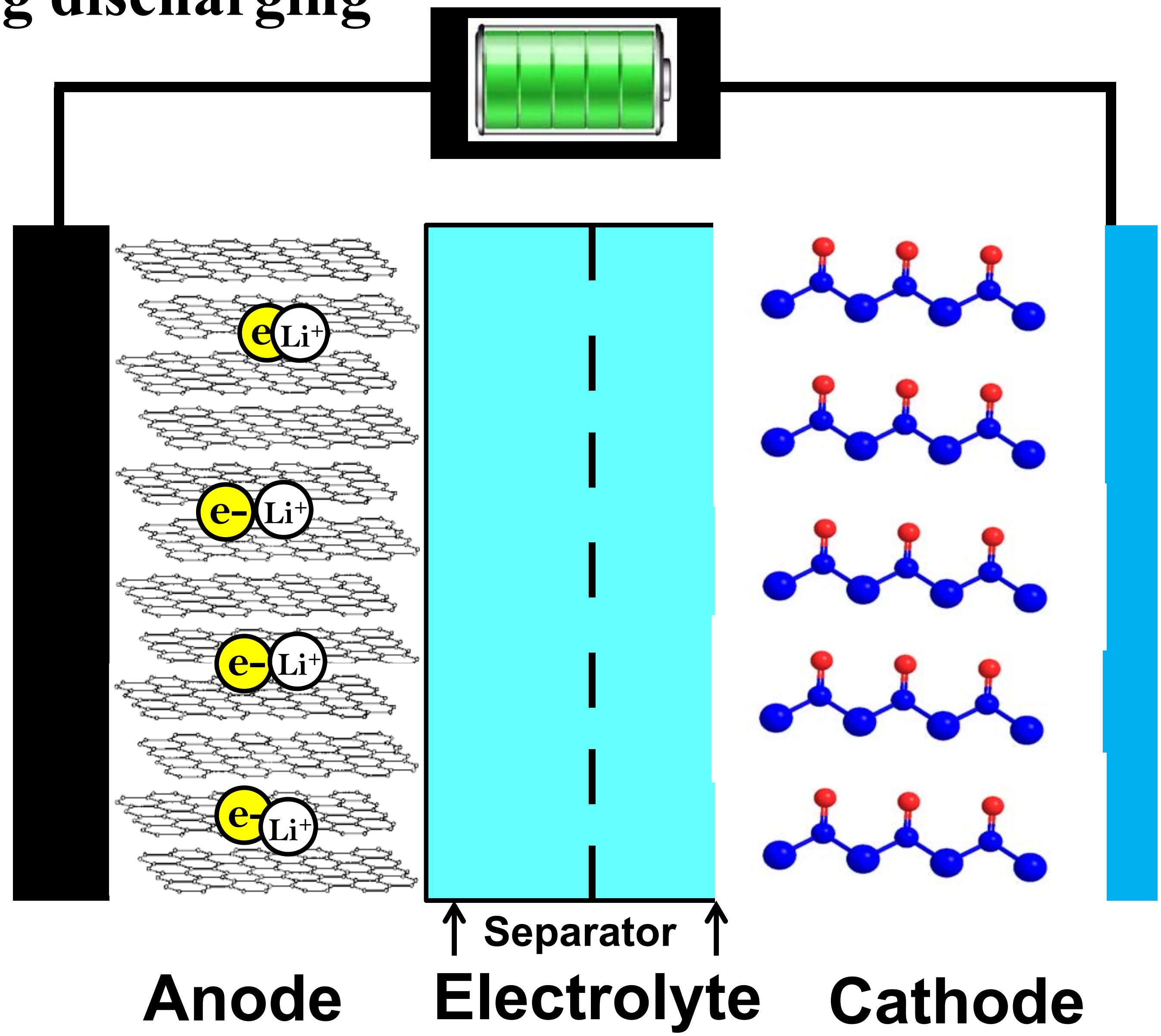
OPERATING PRINCIPLE OF BATTERY

During charging



OPERATING PRINCIPLE OF BATTERY

During discharging



LITHIUM –ION BATTERY : LONGEST IN THE EXPERIENCE CURVE

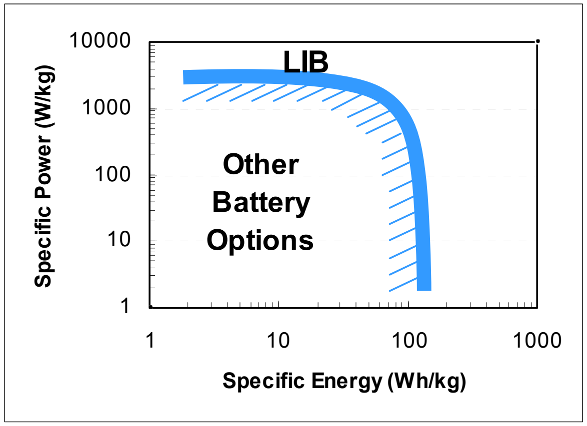
- Two clear fundamental advantages
  1. Lithium is the lightest metal
  2. Lithium half reaction standard electrode potential is big †

$Li^{+} + e^{-} \longrightarrow Li(s) \quad E^{o}(V) \; -3.04V$

- In principal, fundamental advantages could lead to
  - Higher energy density; weight and volume advantage
  - Higher power density at a given energy density
  - Fewer cells, related parts

- Key Hurdles- beginning in 1975
  - Cathode
  - Anode
  - Electrolyte
  - Separator
  - ✓ Self-discharge performance
  - ✓ Memory
  - ✓ Cost per W-h and per W
  - ✓ Abuse resistance
  - ✓ Cold/hot behavior
  - ✓ Thermal management (safety)
  - ✓ Cycle life
  - **Markets?**

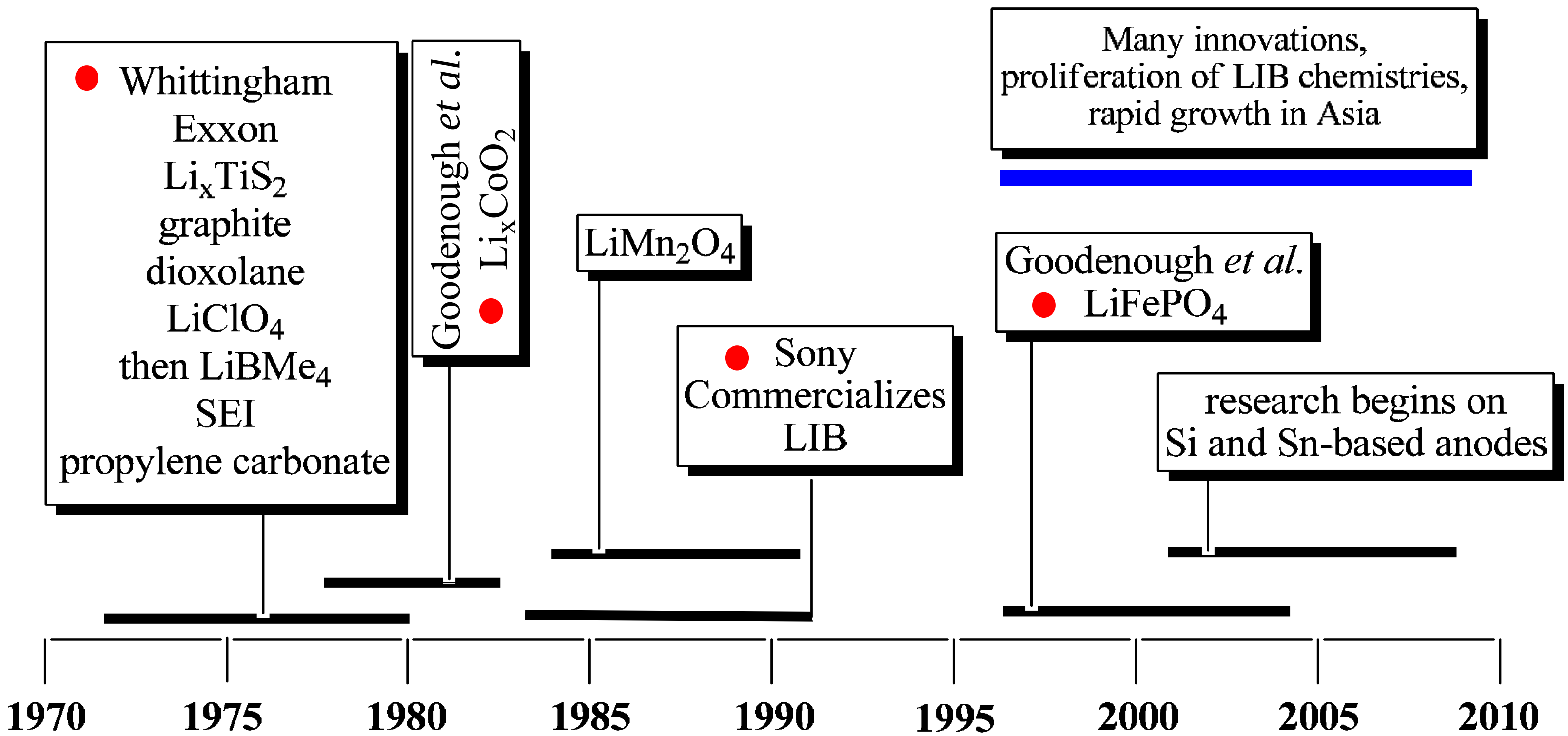
Ragone Plot



* 1 Wh = 3,600 J or 860.4 cal

† *"Electrochemical Series" in Handbook of Chemistry and Physics*

HISTORY AND EVOLUTION OF LITHIUM-ION BATTERY

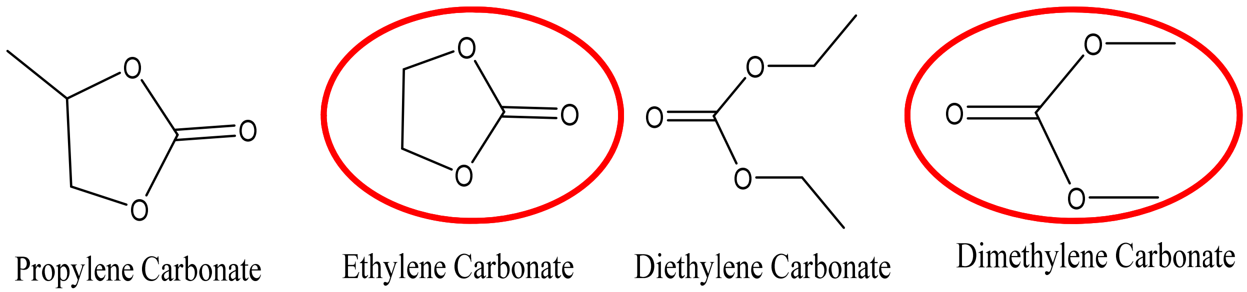


Other Cathodes:
$Li(Ni,Mn,Co)O_2$
$Li(Ni,Co,Al)O_2$

M. S. Whittingham, Chem Rev. 2004, 104, 4271-4301
Y. Nishi in "Lithium Ion Batteries", M. Wakihara and O. Yamamoto, editors 1998
F. Beguin and R. Yazami, Actualite Chimique 2006 295-296, 86-90

THE CRITICAL COMPONENTS OF A LITHIUM-ION BATTERY

- At cathode(positive electrode) : Extraction of lithium ion and creation of large number of vacancies
- At the anode (negative electrode) : intercalation of lithium ions between layers of graphite
- Electrolyte is typically $LiPF_6$ dissolved in a 1:1 mixture of dimethyl carbonate and ethylene carbonate.



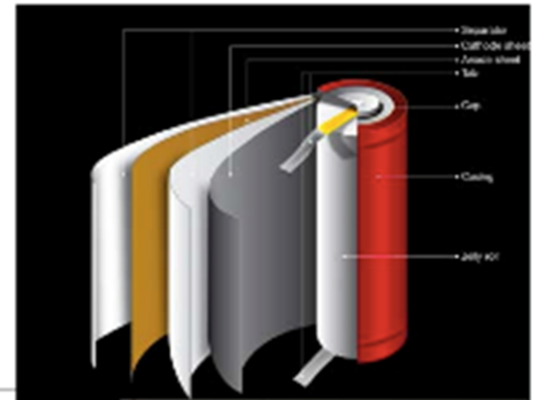
- The separator is a polymer film (membrane) about 25 micron thick, which does not participate "directly" in any electrochemical reaction

DESIRABLE FEATURES OF A BATTERY SEPARATOR MEMBRANE

- Permeable (~40-50% void volume) for ready ion transport, yet insulate electrodes
  - Small pores but low resistance

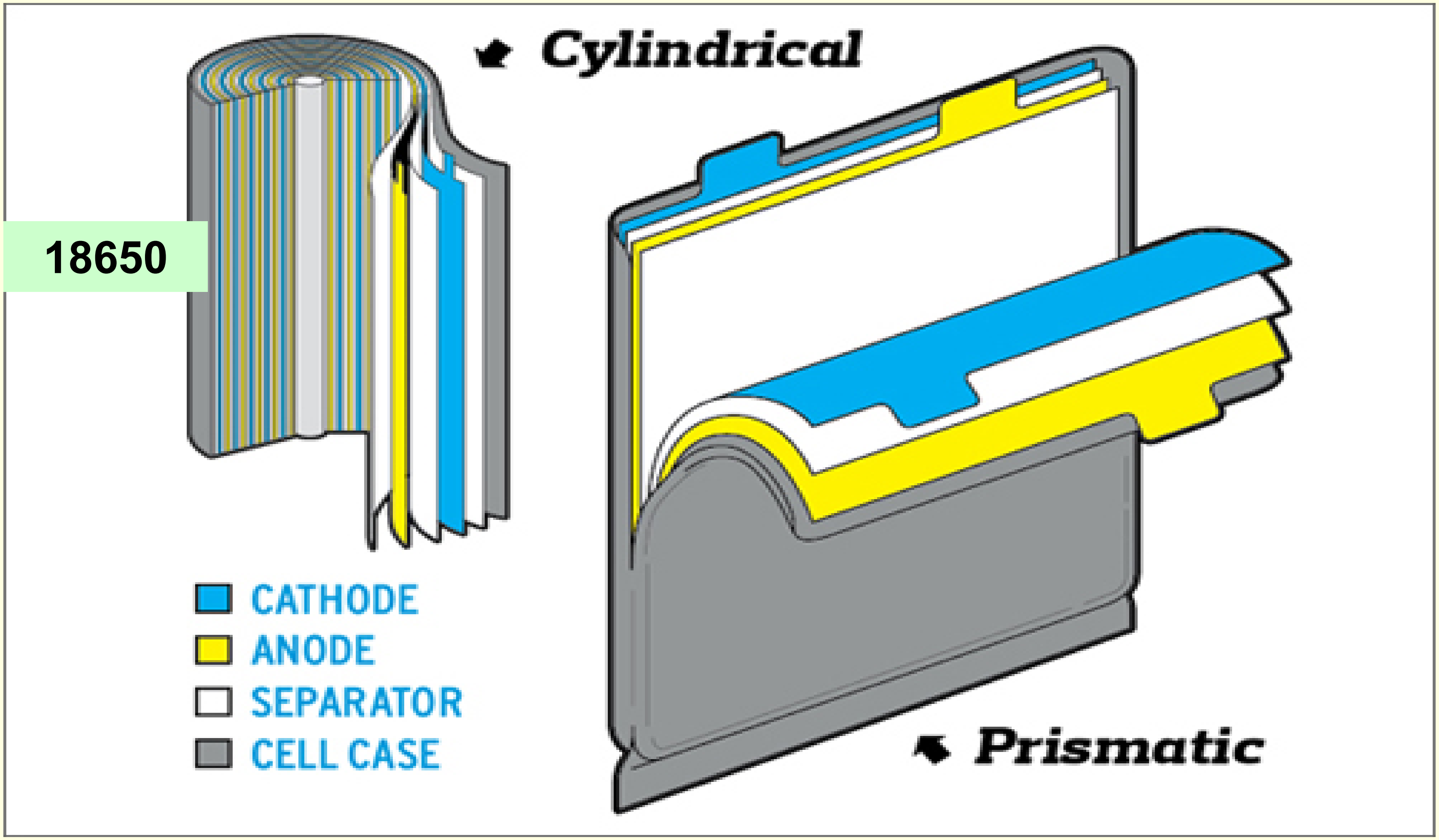
$$R_{eff} \prec \frac{\text{Tortuousity}}{\text{Porosity}}$$

- Chemically inert, uniform, free of flaws
  - 2-10+ years in highly reactive environment
- Excellent puncture strength
  - Thin (7-30μ), dimensionally stable
- Slitting, compatible w/ manufacturing equipment
- Act as safety device if cell becomes too hot
  - Safety margin: Δ = [meltdown temperature – shutdown temperature]
  - The higher the meltdown temperature the better



Lithium dendrite

STANDARD CELL FORMATS

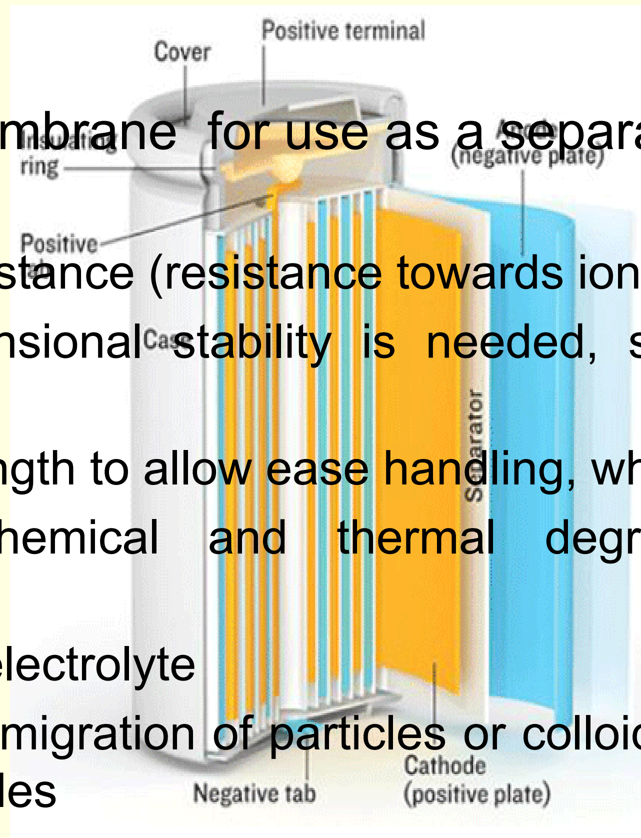


THE POWER BEHIND A TESLA

Tesla uses 18650 standard format cylindrical cells in Model S, 65 mm long and 18.6 mm dia, 7,104 cells per pack giving a total power of 85kWh

SEPARATORS FOR LITHIUM ION BATTERY

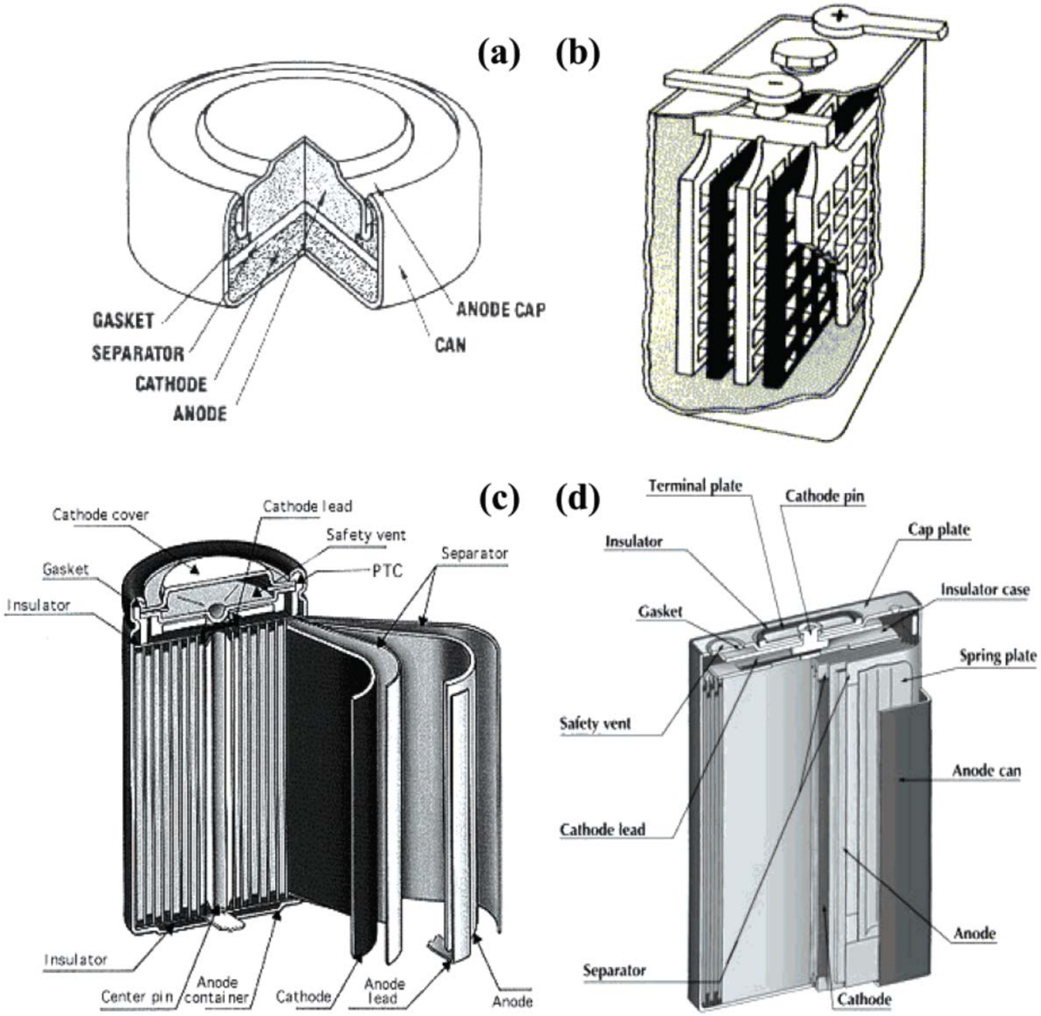
A separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing electric contact of the electrodes.



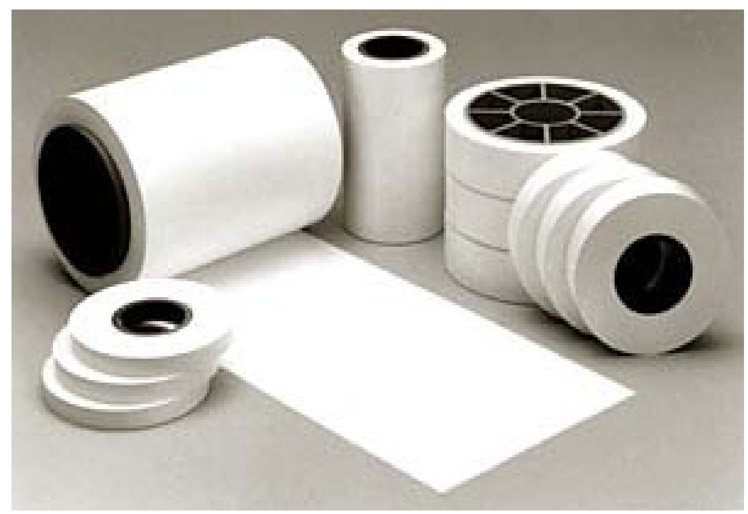
Requirements of a membrane for use as a separator

- Electrical insulator
- Minimal electrolyte resistance (resistance towards ionic flow)
- Mechanical and dimensional stability is needed, so that the structure doesn't collapse
- Sufficient physical strength to allow ease handling, while winding the cell
- Resistant towards chemical and thermal degradation at working temperature
- Readily wetted by the electrolyte
- Effective in preventing migration of particles or colloidal or soluble species between the two electrodes

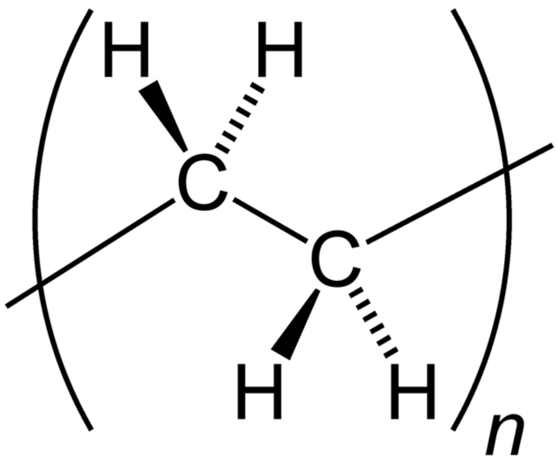
POROUS POLYMERS FOR SELECTIVE TRANSPORT OF LITHIUM IONS



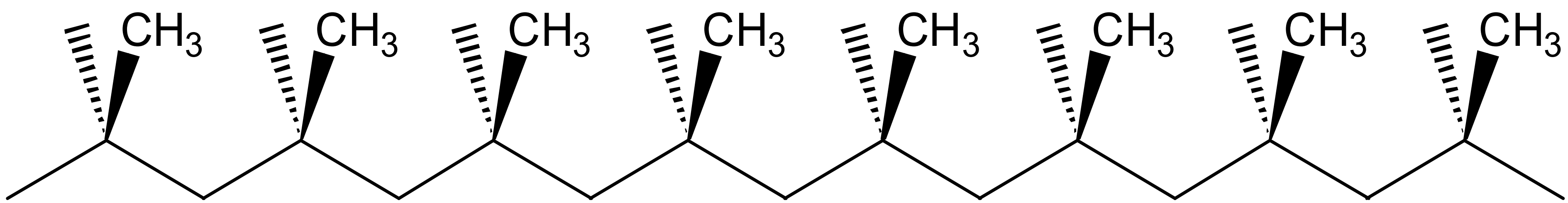
Current material of choice : Polyolefins



POLYETHYLENE AND POLYPROPYLENE

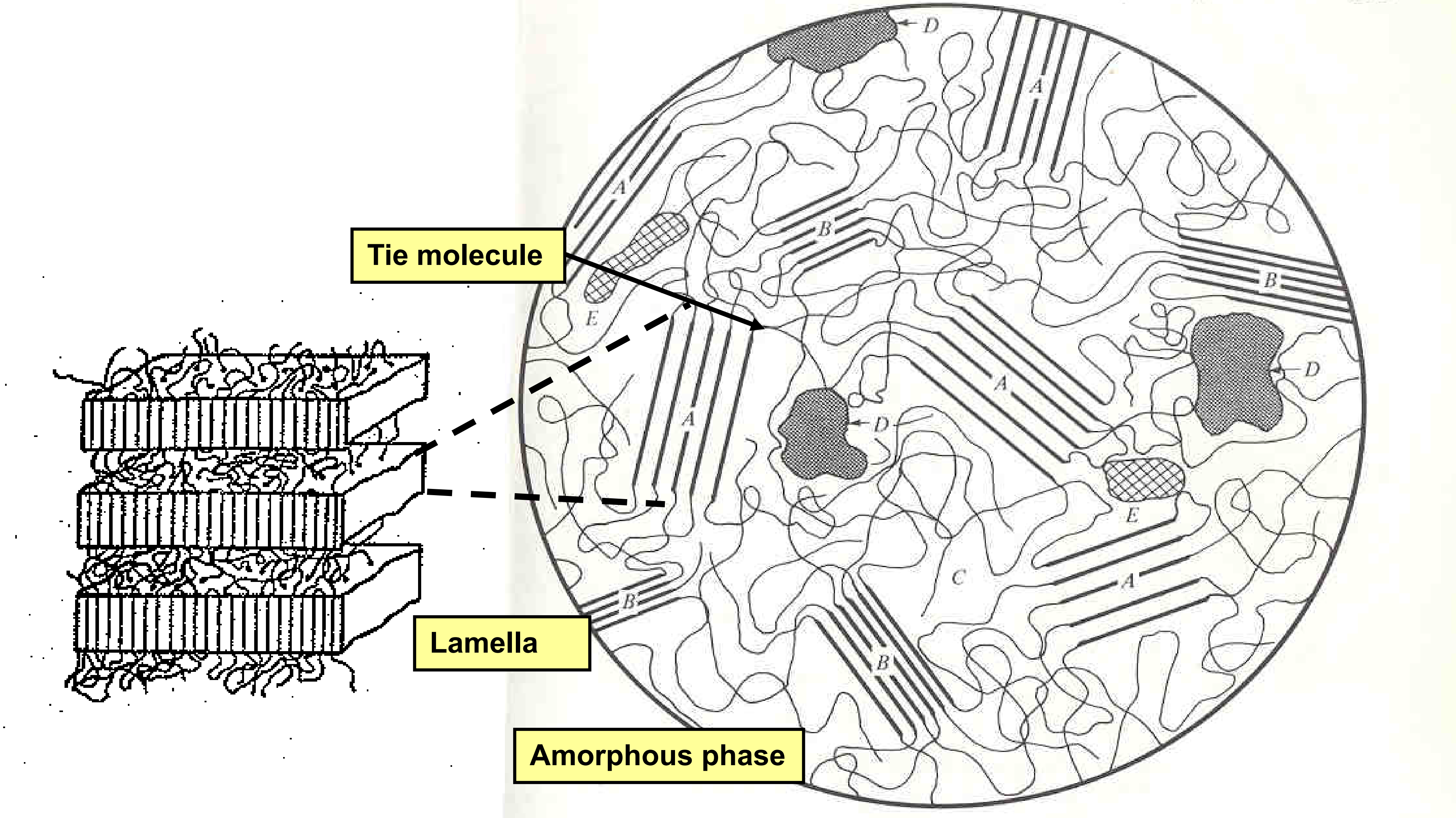


Polyethylene repeat unit
Semicrystalline
Tm : 135-140° C



Isotactic-Polypropylene chain
Semiccrystalline, Tm : 160 ° C

TYPICAL MORPHOLOGY OF A SEMI-CRYSTALLINE POLYMER SHOWING FRINGED MICELLE STRUCTURE

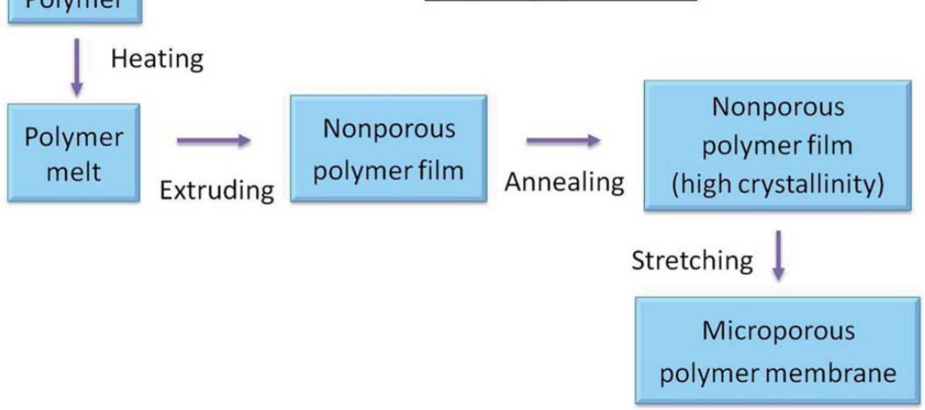


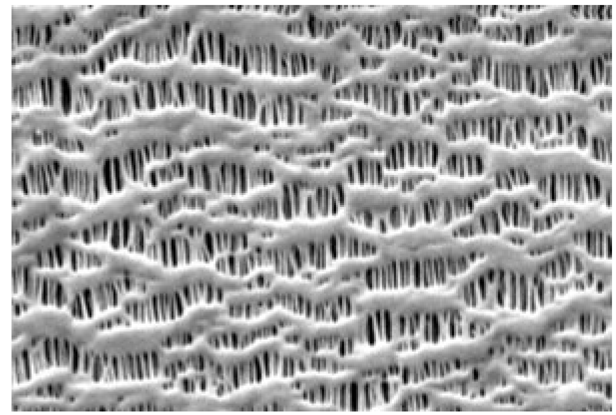
(b)

Figure 4.1. (Cont.)
(b) Copolymer:

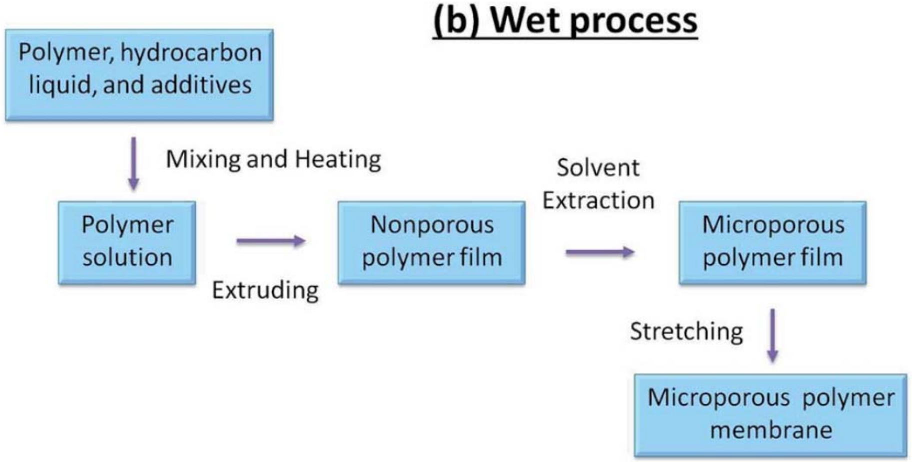
PROCESSES USED FOR MAKING POLYOLEFIN SEPARATORS

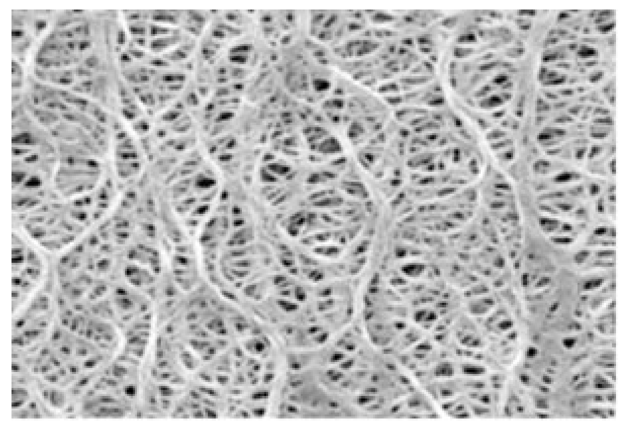
(a) Dry process





(b) Wet process





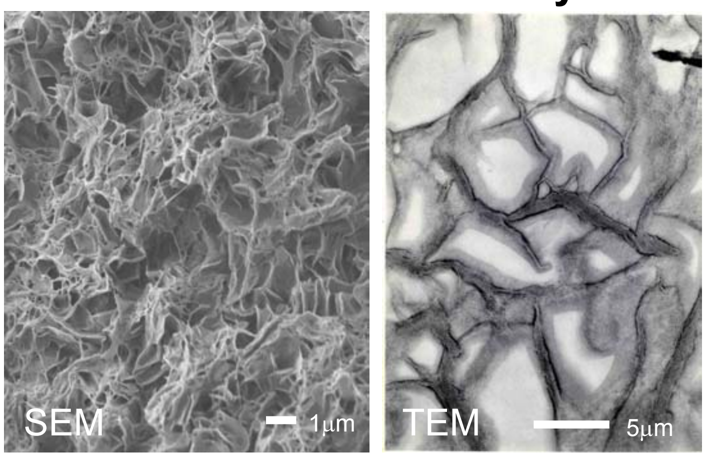
MICROPOROUS PE SEPARATOR USING GEL SPINNING

- Pennings et al, 1965 - 1979: Gel spinning and super drawing of uhmw HDPE filaments

Solution of polyethylene dissolved in hydrocarbon

Gel sheet

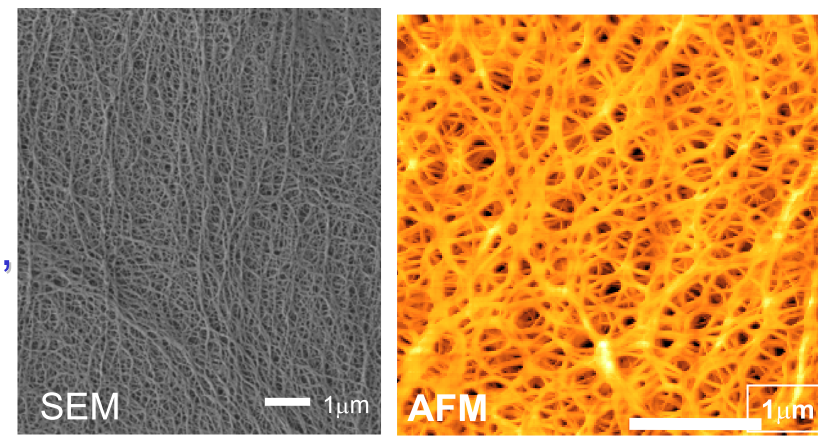
Thin wall cellular structure composed of stacked lamella crystals



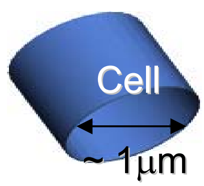
Biaxial orientation, extraction

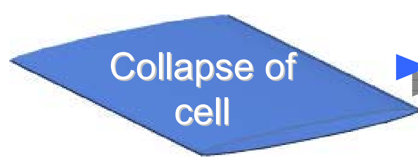
Micro-porous film

Uniform fine fibrous network composed of stacked lamella crystals

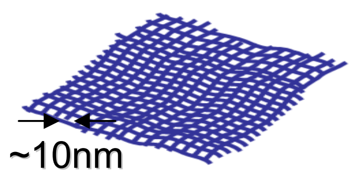


Schematic diagram

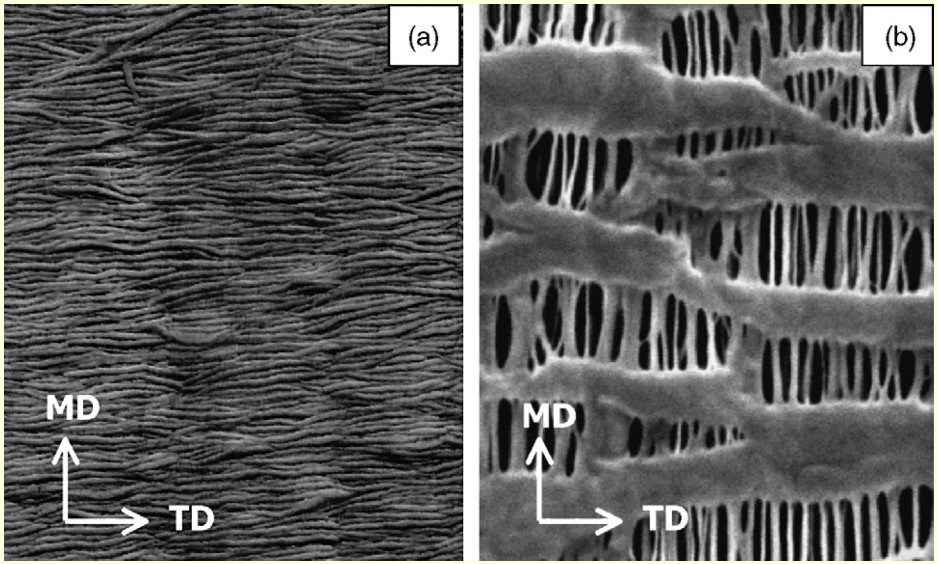




Fibrillation of plane stacked lamella crystal



POROUS HDPE FILM BY EXTRUSION AND STRETCHING



Before stretch After stretch

- Cold Stretch: Stretching the film in the machine direction at low temperature with a fast strain rate
- Hot stretch : Stretching at high temperatures with a lower strain rate

Uniaxial stretching: Stretching only in the machine direction
Biaxial stretching : Stretching in machine and transverse directions

COMMERCIALLY AVAILABLE SEPARATOR MEMBRANES

Table I. Commercial separator properties.*

	Entek	Exxon	Degussa	Celgard
Product	Teklon	Tonen	Separion	2325
Thickness (μm)	25	25	25	25
Single/multilayer	Single layer	Single layer	Trilayer	Trilayer
Composition	PE	PE	Ceramic-PET-Ceramic	PP-PE-PP
Process	Wet extruded	Wet extruded	Wet-laid mat	Dry extruded
Porosity (%)	38	36	>40	41
Melt temperature	135	135	220	134/166

* Separator specifications are found on data sheets for each product

Lower the thickness, lower the resistance resulting in high energy and power density

PORE MORPHOLOGIES OF SOME COMMERCIAL SEPARATOR MEMBRANES

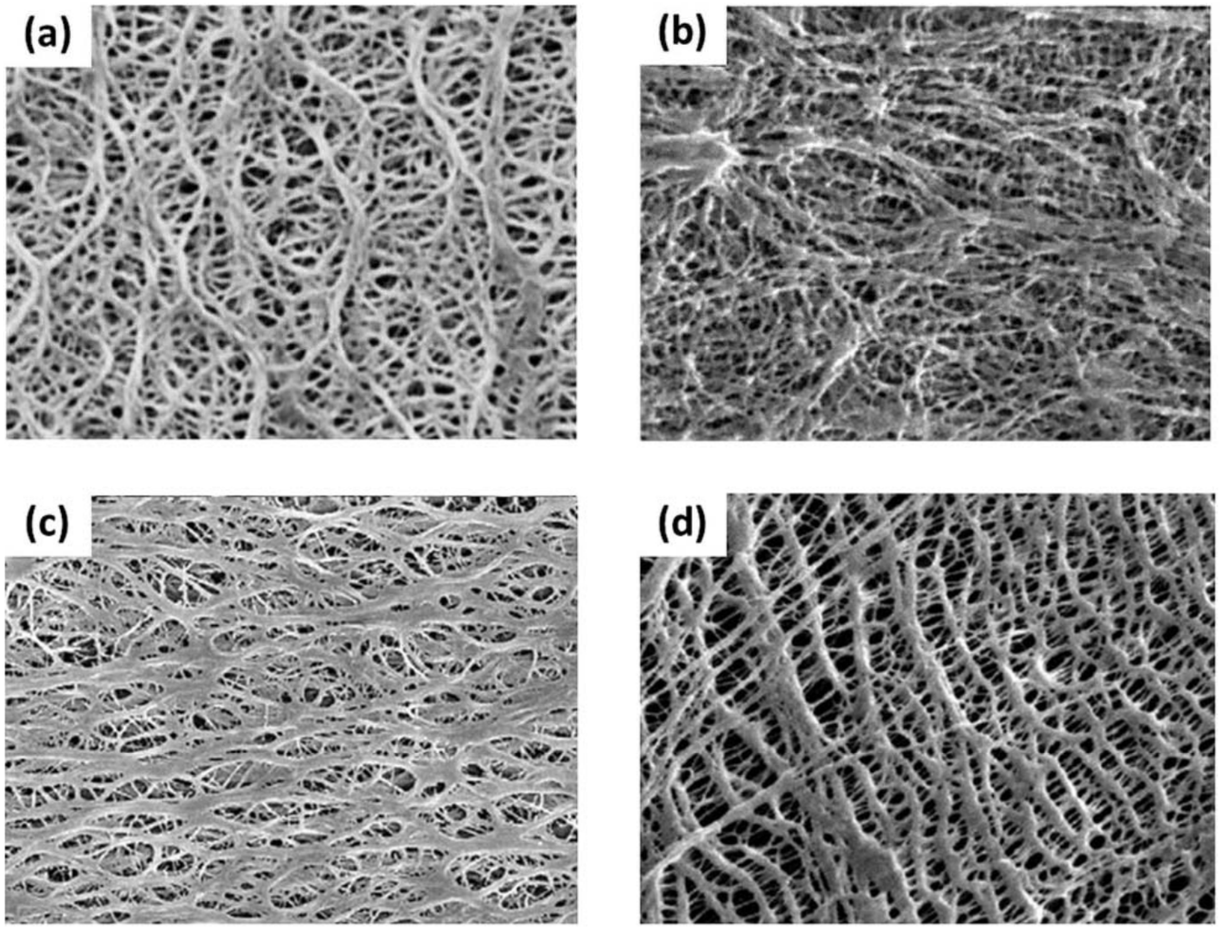
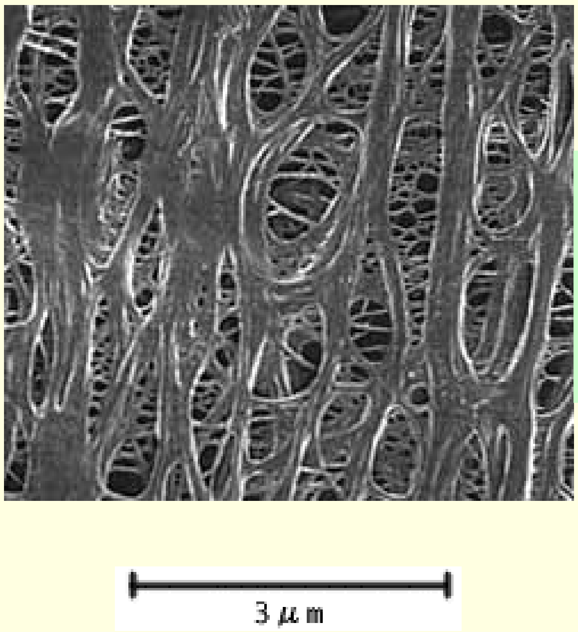
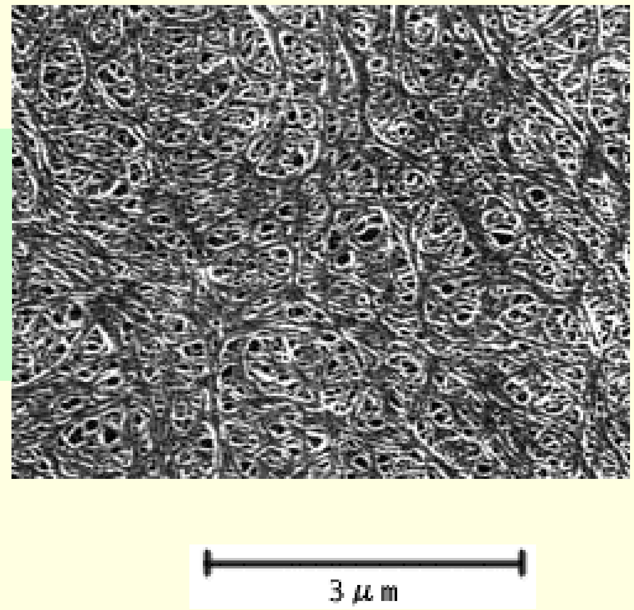


Fig. 5 SEM images of microporous membrane separators prepared by a wet process: (a) Celgard,[41] (b) Tonen,[6] (c) Asahi,[41] and (d) Entek.[6] Reproduced with permission.

PORE MORPHOLOGIES OF SOME COMMERCIAL SEPARATOR MEMBRANES



Typical pore size: < 1 micron



Large Pore diameter HiPore™ : Source: http://www .asahi-kasei.co.jp/hipore/en

Small Pore diameter HiPore™ ; Source : http://www.asahi-kasei.co.jp/hipore/en

Large pore size material absorbs more electrolyte resulting in high ionic conductivity, but has low mechanical strength; small pore size results in insufficient electrolyte absorption

POLYOLEFIN MEMBRANES ARE NOT THE MOST IDEAL MATERIALS FOR SEPARATORS

•Polyolefins are hydrophobic and, hence, intrinsically less compatible with liquid electrolytes ; have low retention capacity to hold organic solvents with high dielectric constant

•PO separators have poor wettability characteristics in polar electrolytes, such as, ethylene carbonate (EC), propylene carbonate (PC), and γ-butyrolactone (GBL) owing to their low polarityPO separators have poor wettability characteristics in polar electrolytes, such as, ethylene carbonate (EC), propylene carbonate (PC), and γ-butyrolactone (GBL) owing to their low polarity.

•Polyolefins have a Tm ~ 150 to 160° C ; Pores tend to collapse near Tm, causing shrinkages and shorting

•Polyolefins are also flammable

Samsung Slumps by $22 Billion as Note 7 Safety Warnings Pile Up

Stepping up its warnings, the world's largest smartphone mak
users worldwide to immediately turn the device off and bring

Seoul: Samsung Electronics lost $22 billion of market value over two days as investors factor in a bigger hit to its bottom line from widening bans and warnings on its Note 7 smartphones.

Shares have plunged 11% since Friday, the biggest two-day decline since 2008, after US regulators joined the company in cautioning users to power down their Note 7s and refrain from charging them. Aviation authorities and airlines have called on passengers to stop using the gadgets during flights...

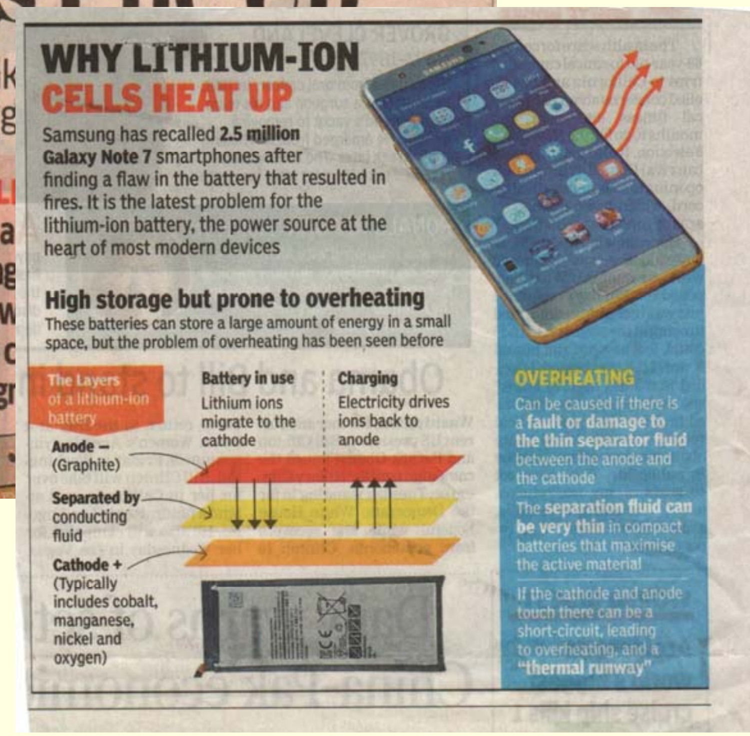
Samsung told users in South Korea to stop using the devices and to bring them to its service centres — less than a month after they made their debut.

Note 7s with new batteries are due to become available on September 19. The Suwon, South Korea-based company has said about 2.5 million had been shipped before their recall, including those in the hands of consumers and carriers.

The US Consumer Product Safety Commission and Samsung are in talks on an official recall of the devices as soon as possible. Almost...

NOTE 7 RECALL

The recall dealt a
blow to Samsung
tation at a time w
faces a growing c
in all market segr



WHY LITHIUM-ION CELLS HEAT UP

Samsung has recalled **2.5 million Galaxy Note 7** smartphones after finding a flaw in the battery that resulted in fires. It is the latest problem for the lithium-ion battery, the power source at the heart of most modern devices

High storage but prone to overheating

These batteries can store a large amount of energy in a small space, but the problem of overheating has been seen before

OVERHEATING

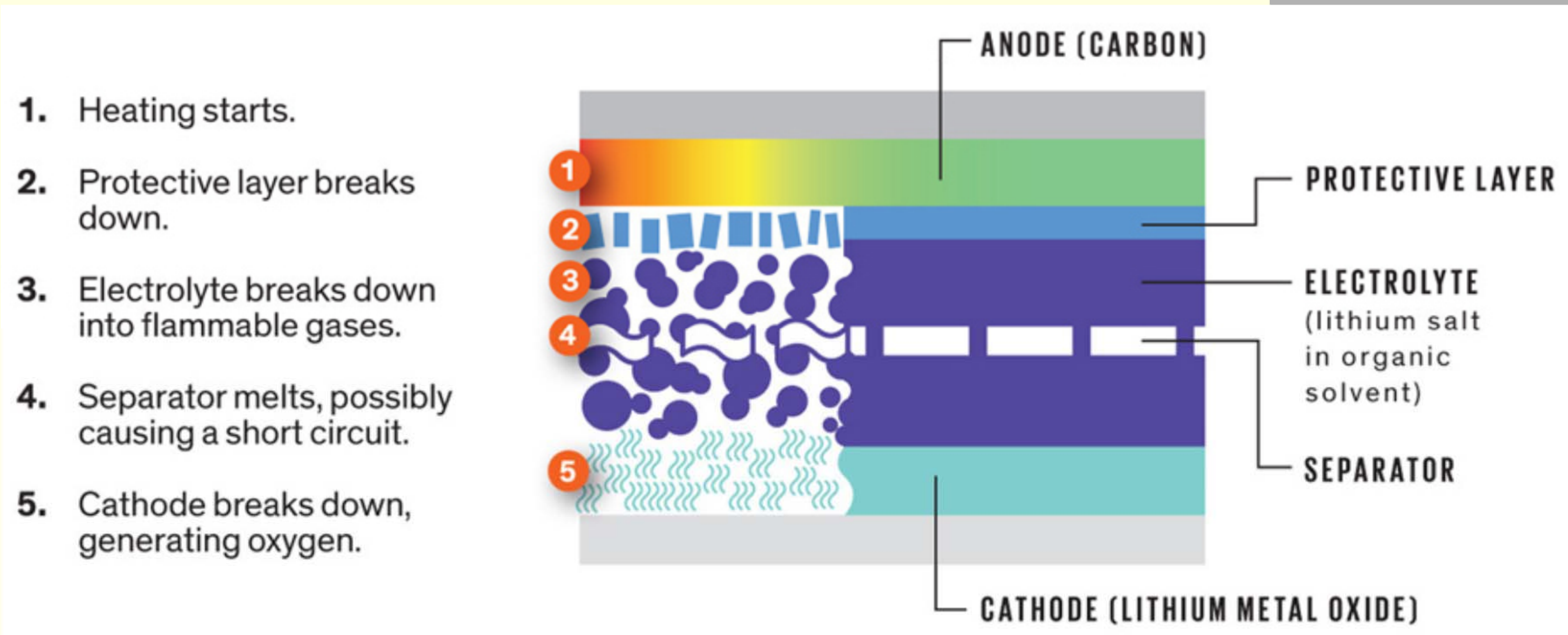
Can be caused if there is a **fault or damage to the thin separator fluid** between the anode and the cathode

The **separation fluid can be very thin** in compact batteries that maximise the active material

If the cathode and anode touch there can be a short-circuit, leading to overheating, and a **"thermal runway"**

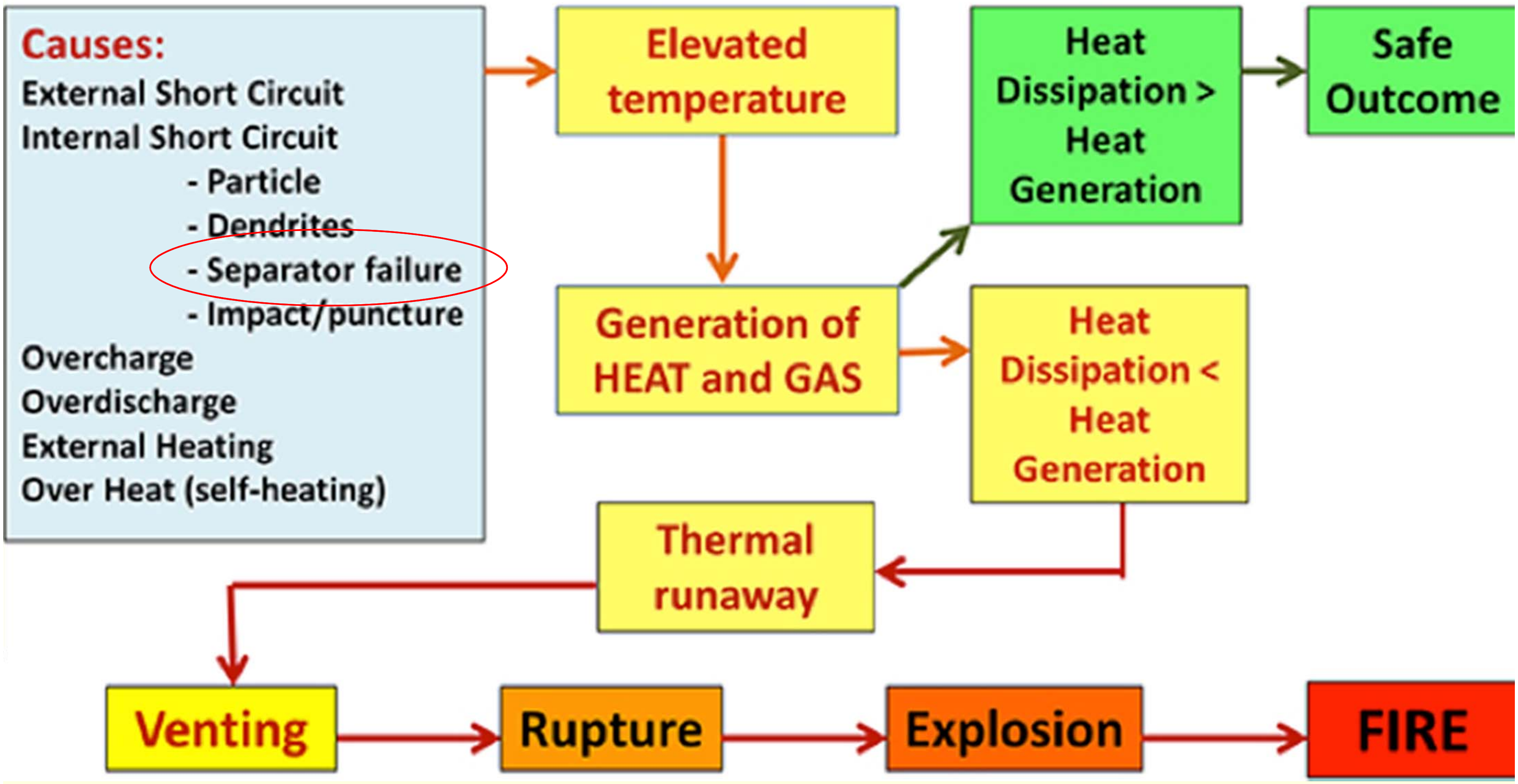
WHY DO LITHIUM ION BATTERIES CATCH FIRE ?

(Chemical and Engineering News, 94(45), November 14, 2016)



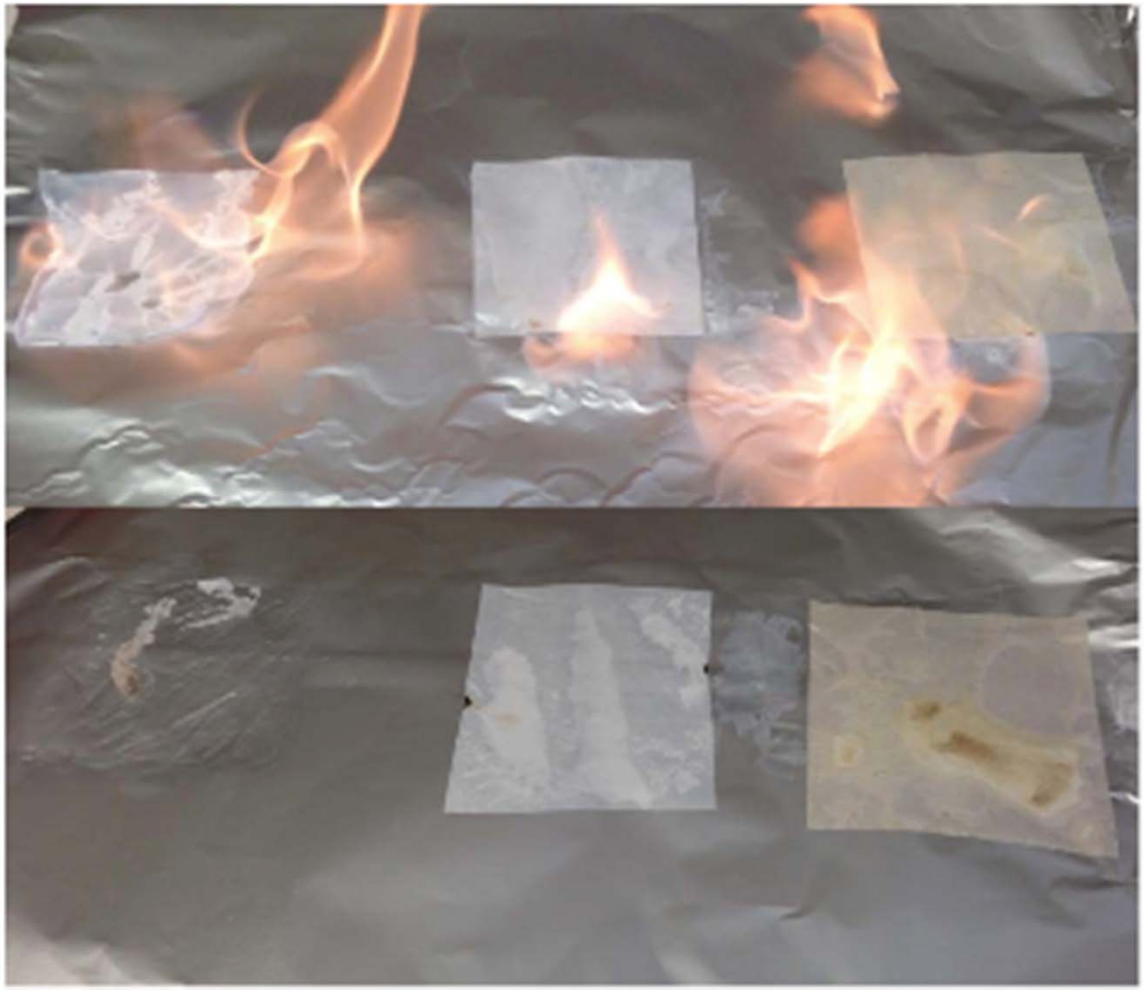
- ✓ Predominant materials used for separators : Polypropylene or polyethylene (Polyolefins)
- ✓ Crystalline polymers which undergo shrinkages above 120 C
- ✓ Typical separator thickness ~ 50 microns; but tendency to reduce the thickness to increase energy and power density; current thickness is approaching 20 microns

Anatomy of Cell Failure



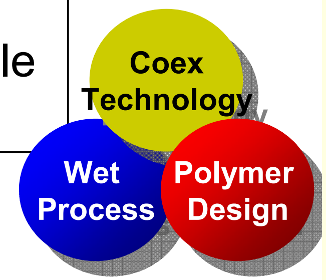
At 100-130° C cathode is a source of oxygen. When overcharged, oxygen is released which causes the flammable electrolyte to ignite

POLYOLEFIN SEPARATOR MEMBRANES ARE ALSO FLAMMABLE !



DESIRABLE FEATURES OF AN IDEAL BATTERY SEPARATOR MEMBRANE MATERIAL

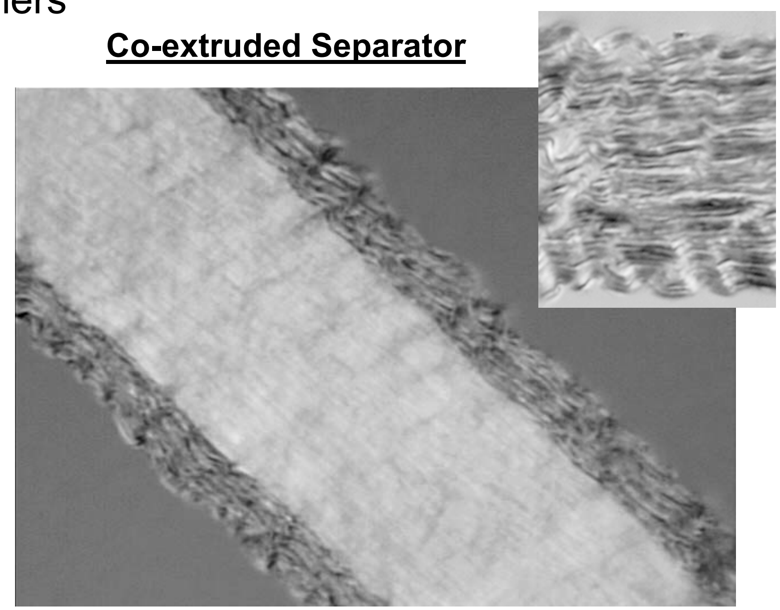
for larger battery formats, and bigger battery packs….
but emphases vary according to LIB chemistry and module or pack control



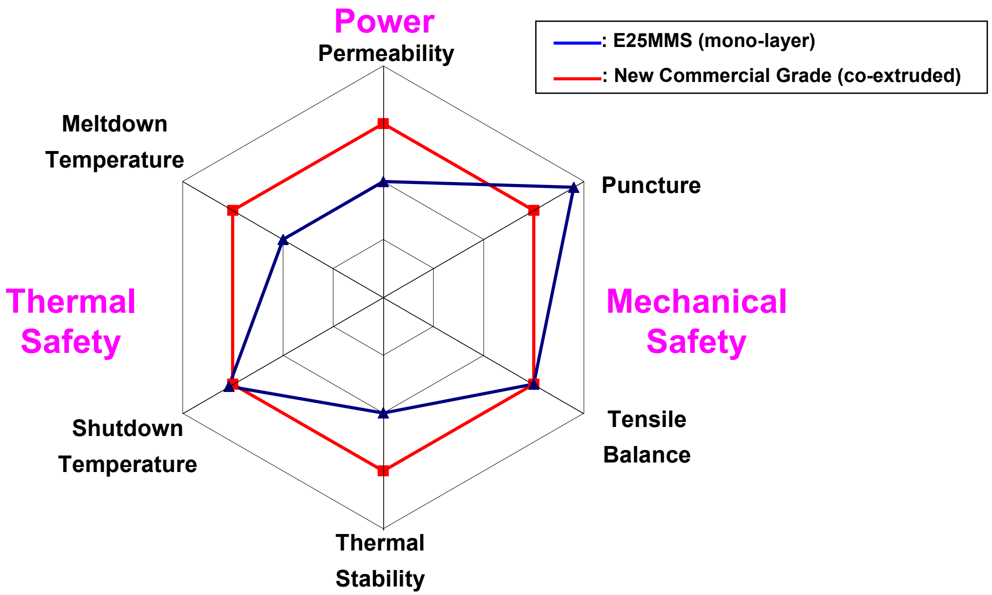
- Higher temperature stability - ~ 200-250+C
  - Retain sufficient dimensional stability
  - Coatings and higher temperature polymers
    - Blends, co-extrusion
- Increasing puncture resistance
  - w/ appropriate permeability
- Lower shutdown temperature
- ~10+ year life
- Delivered flawlessly at lower cost

Monolayer

Co-extruded Separator

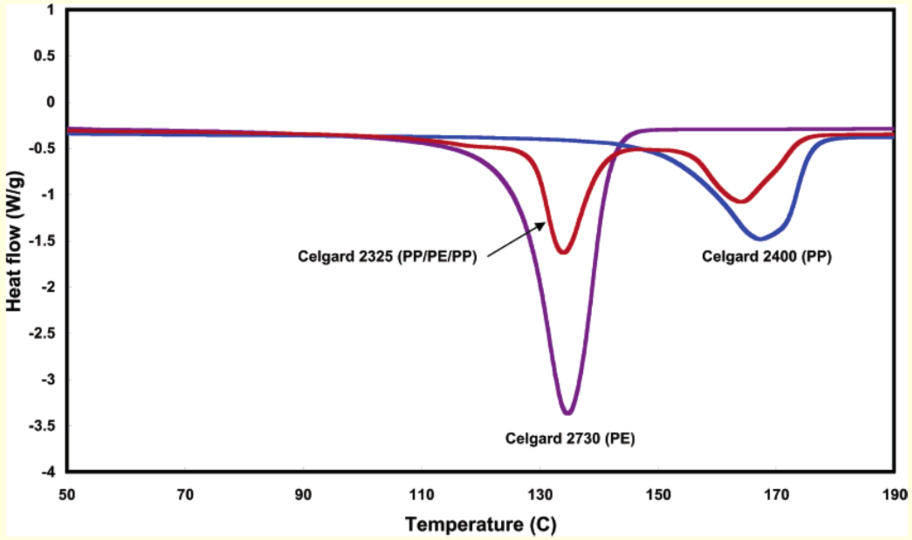


SINGLE VS TRI-LAYER SEPARATOR MEMBRANES



New commercial grade has superior thermal stability, higher permeability and meltdown temperature than standard mono-layer

DSC of single layer PE, PP and trilayer PE-PP-PE



INCREASING ENERGY DENSITY, QUICKER CHARGING MAKES NEW DEMAND ON BATTERY SEPARATOR MATERIALS

- Chemical stability
- Film thickness : Power density
- Uniform pore size : Uniform current density
- Tortuosity: Suppress dendritic lithium formation
- Wettability to polar electrolytes
- Low thermal shrinkage

Specific Energy is currently at 650 -700 kWh/L,
Up from 200 -300 in mid nineties

To improve battery performance, separators have been made thinner diminishing their capability to perform critical functions such as preventing electrode contact, resisting puncture by lithium dendrites and shutting the battery off when overheating occurs

IMPROVING SEPARATOR PERFORMANCE

- Ceramic reinforced polyolefin separators
- Ceramic coating on polyolefin separators
- Surface modification of polyolefins with polar and wettable functional groups
- Amorphous functional aliphatic polymers such as poly(vinylidene fluoride), poly(acrylonitrile)
- Amorphous , high Tg aromatic polymers with polar functionalities
  - Polyimides
  - Polybenzimidazoles

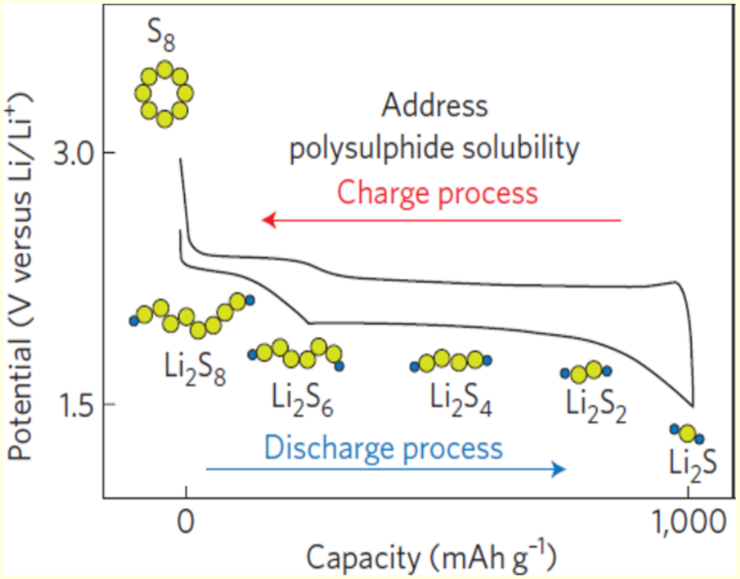
LITHIUM-SULFUR BATTERY

- One of the most abundant elements on earth, Sulfur potentially accepts up to two electrons per atom, at ~2.1 V vs. Li/Li^+ .
- So sulfur cathode materials show the highest theoretical capacity among the solid elements, numerically 1675 $mAh^{-1}g$, attributing very high theoretical energy density of ~2600 $Whkg^{-1}$ to lithium-sulfur batteries.
- Besides having higher energy density, the low operating voltage 2.15V vs. Li/Li^+ ensures greater safety.
- Sulfur is non-toxic and cheap because of its higher abundance than the expensive transition metals routinely used in the Li-ion batteries.

System	Theo. Energy density ($WhKg^{-1}$)
Li ion	100-265
Li-S battery	2510
$Li-O_2$ (air)	12000 1700 (reported)
Na^+ ion	400
$Mg-O_2$ (air)	6800

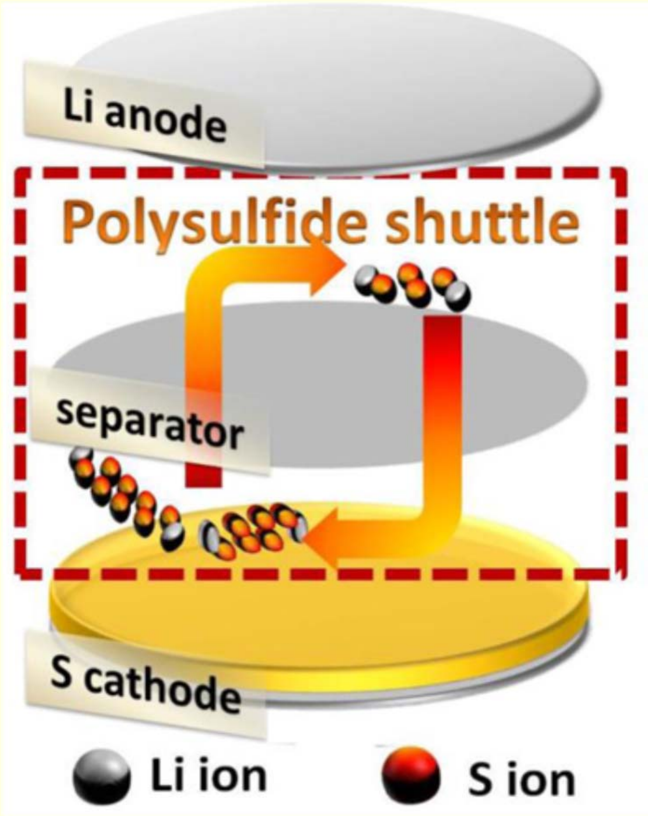
LI-S BATTERY : PRINCIPLES

- During an ideal discharge process, cyclo-S_8 is reduced and accommodates two Li atoms, to form the high order lithium polysulfides Li_2S_x ($6<x\leq 8$). Then it is further reduced incorporating other Li atoms, forming lower order polysulfides Li_2S_x ($2<x\leq 6$).
- So, in ether based electrolytes, two discharge plateaus are observed, in 2.3 and 2.1V representing conversion of S_8 to Li_2S_4 and Li_2S_4 to the end product, Li_2S. The reaction is reversible under charge-discharge conditions.



THE SHUTTLE EFFECT AND THE ROLE OF SEPARATORS

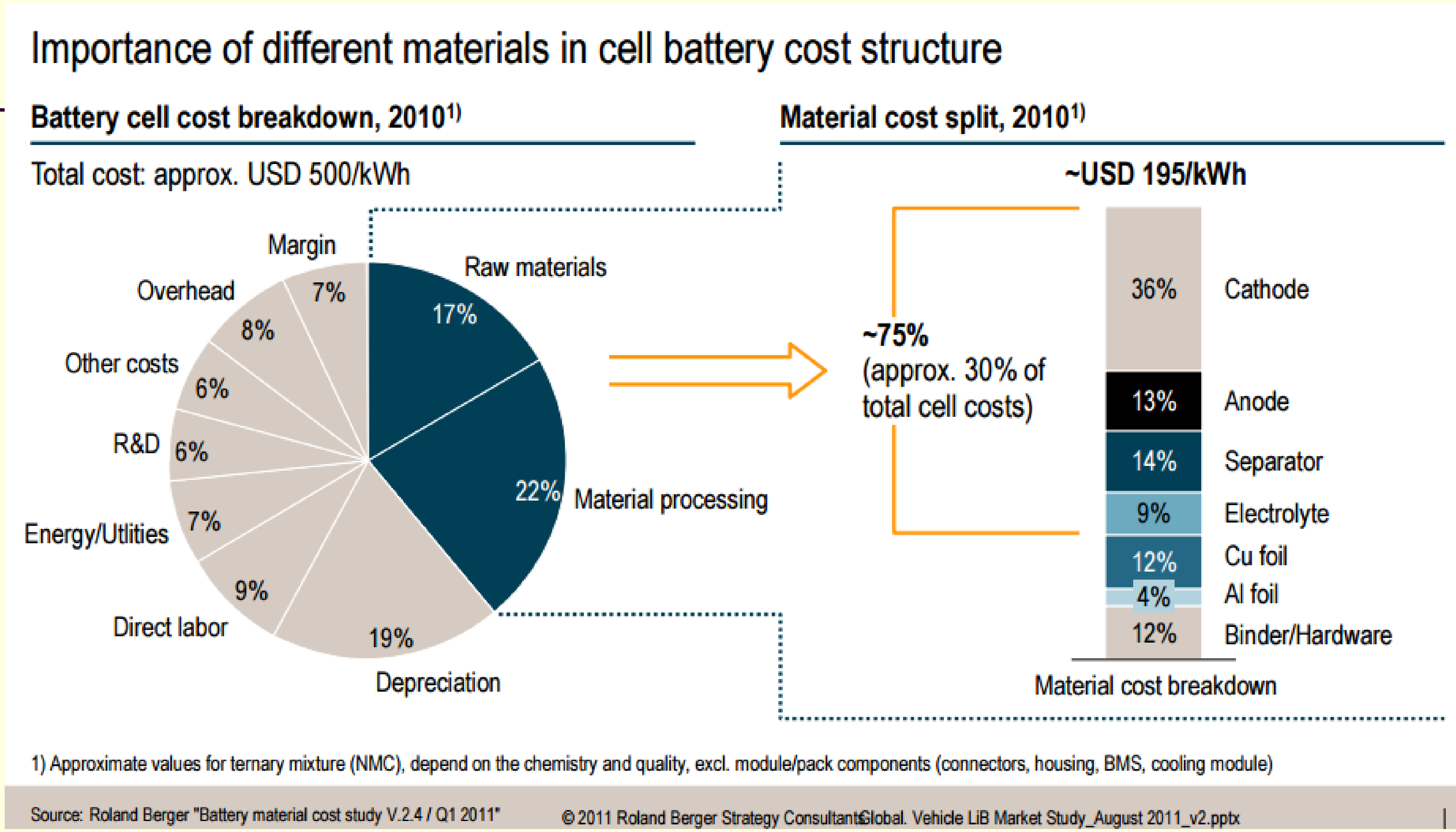
- The multi-electron mobile redox centers of the soluble polysulfides, Li_2S_x ($3<x\leq8$) leads to severe capacity degradation, lowered Coulombic efficiency and poor cyclic life.
- The soluble polysulfides diffuse across the separator, and participate in parasitic redox reactions with elemental sulfur and metallic lithium, thus consuming active materials without energy output.
- Again, the insoluble Li_2S and Li_2S_2 is deposited on the anode, increasing internal resistance



SEPARATOR MEMBRANES FOR LITHIUM-S BATTERIES

- The separators currently used for lithium-ion batteries cannot be used for Lithium –S batteries
- This is because polyolefin type membranes are not selective only to lithium ions in presence of polysulfide anions
- Suitable modification of the separator membrane surface to restrain the diffusion of polysulfide ion and containing the shuttle effect is needed
- Robust and viable solutions for accomplishing this is still not available

THE COST OF SEPARATOR IN A BATTERY IS NOT TRIVIAL



The current value of the separator market is about 20 % of the lithium –ion battery component market and is valued at about $ I billion

SPECIFICATIONS FOR THE NEXT GENERATION SEPARATOR

Property	Value	Units	Test Method
Melting temperature, T_m	> 220	°C	ASTM D3418
Air permeability	< 150	sec/100 mL of air	JIS 8117
Pore size	< 30	nm	ASTM F316-03 (Mean flow pore size)
Porosity	> 40	%	By calculation (see note 1)
Tensile strength	> 1000	kg/cm^2	ASTM D882-02
Thickness, t	< 20	μm	JIS K7130-99
Chemical resistance	Little or no degradation when exposed to lithium salts in organic solvents such as ethylene carbonate, dimethyl carbonate, and diethyl carbonate		
Flexibility	Separator could be enrolled with metal foil electrodes. Separator should not be broken during assembly of a cell. Separator could be subject to some pressure after rolling.		

Note 1) $Porosity(\%) = \left(1 - \frac{\frac{m_{sample}}{V_{sample}}}{\rho_{material}}\right) * 100\%$ where m_{sample} and V_{sample} are the mass and volume of the separator sample, respectively, and $\rho_{material}$ is the (bulk) density of the material used to construct the separator.

THE JOURNEY IS NOT COMPLETE

TODAY	***FUTURE***
100 W h/Kg	250 W h/Kg
200 W h/L	400 W h/L
$500/kWh	$125/kWh

HEV	16 kWh	64 Km
EV	30 kWh	250 Km
EV	**60 kWh**	**500 Km**

READING MATERIALS

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THANK YOU FOR YOUR PATIENT LISTENING