Safety and Gel Membranes for Lithium Ion Batteries

Prof. Dr. Yuping Wu

New Energy and Materials Laboratory (NEML),
Department of Chemistry,
Fudan University, Shanghai 200433, China
Tel/Fax: +86-21-5566 4223
Email: wuyp@fudan.edu.cn

@ANL, US-China Workshop, 31st August, 2010

Motto of NEML

4E

Electrochemical knowledge

Solve

Reduce

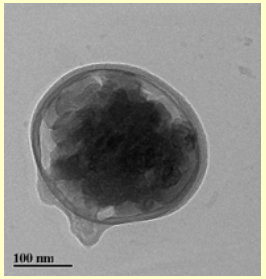
Energy problem

Environmental pollution

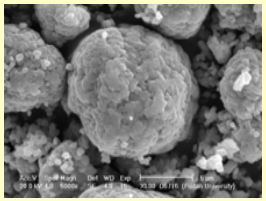
better Enjoy of life

NEML

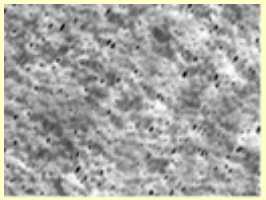
- Lithium ion batteries
  - Anode materials
  - Cathode materials
  - Electrolyte additives
  - Gel membranes
  - Manufacturing tech.



Core-shell



$Li[CoNiMn]O_{2-x}A_x$



Porous membrane

60 Ah LIB

- Aqueous rechargeable lithium batteries(ARLBs)
- Supercapacitors: Hybrid ones such as $AC//Na(K)MO_x$
- Other new power sources
- Solar hydrogen ⟶ To prepare hydrogen by solar energy to split water.

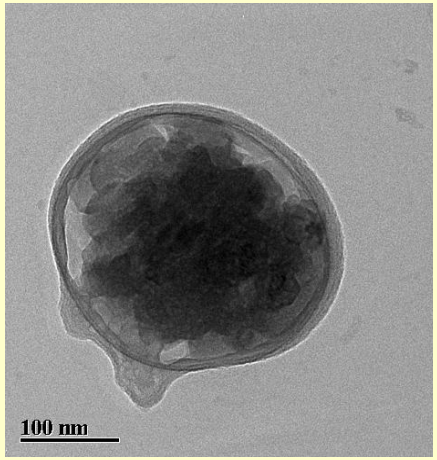
Unique findings on core-shell structured anode materials

monomer → Polymerization → Nano particles → Heat treatment → Core-shell

Polymer shell

Polymeric carbon shell

Unique synthesis scheme:
polymer chemistry



TEM micrograph of core-shelled TiO_2-C nanocomposites.

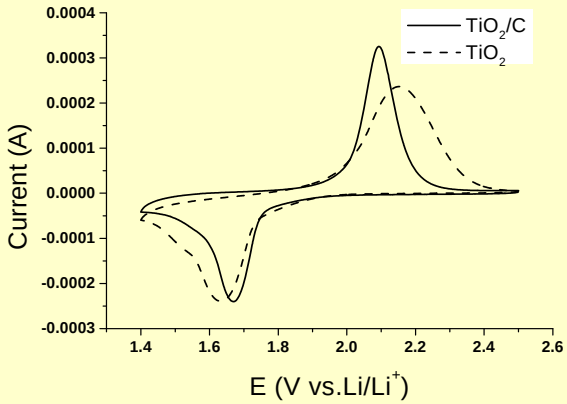


Fig. CVs of TiO_2 and TiO_2/C electrodes measured at the range of 1.4 -2.5V at the scanning of 0.1mV/s.

- **Prevent aggregation**
- **Improved kinetics:**

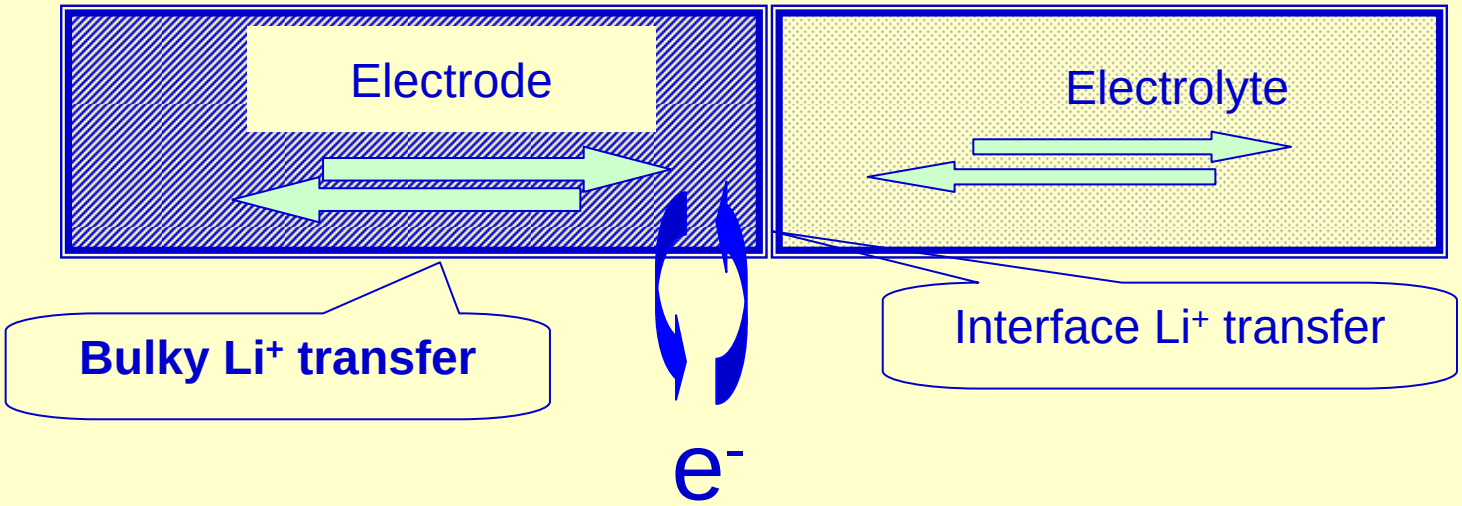
The diffusion coefficient of Li^+ in TiO_2/C (1.07×10^{-8} cm^2/s) is about one order of magnitude higher than that in TiO_2 (1.97×10^{-9} cm^2/s).

Carbon shell

Prof. Besenhard

Convincing theoretical explanation

Two processes during charge and discharge



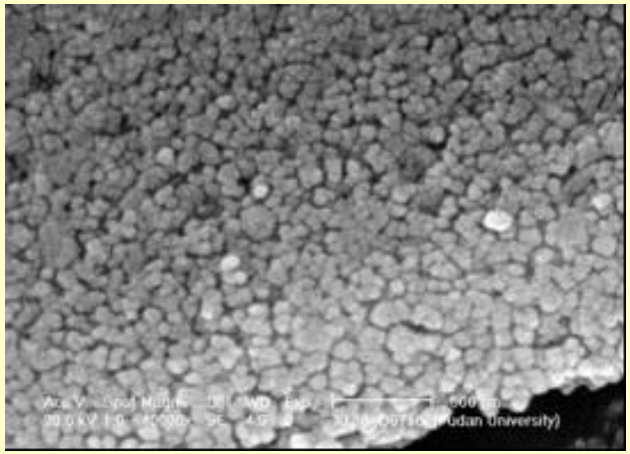
$$\sigma^{\delta} = \frac{\sigma_{electron} \cdot \delta_{ion}}{\sigma_{electron} + \sigma_{ion}}$$

One process will favor the another process, and the total process is greatly favored. Just like a team.

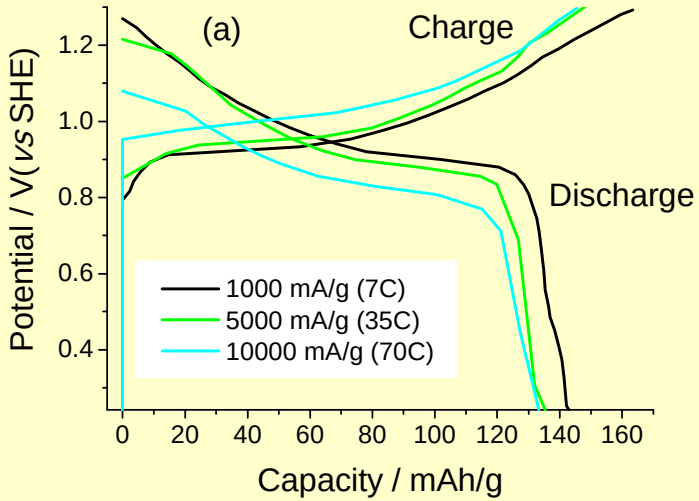
Wu et al., *Electrochem. Commun.*, 8, 1 (2006).

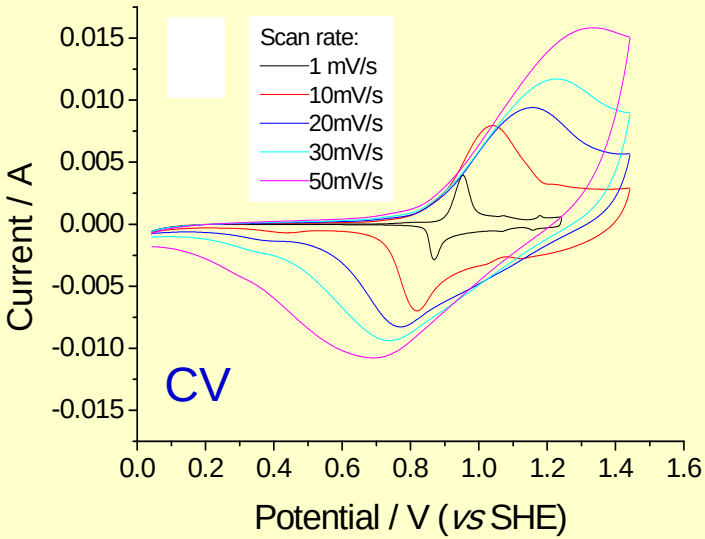
Excellent rate performance of $LiCoO_2$ in aqueous solutions

Patented.



SEM

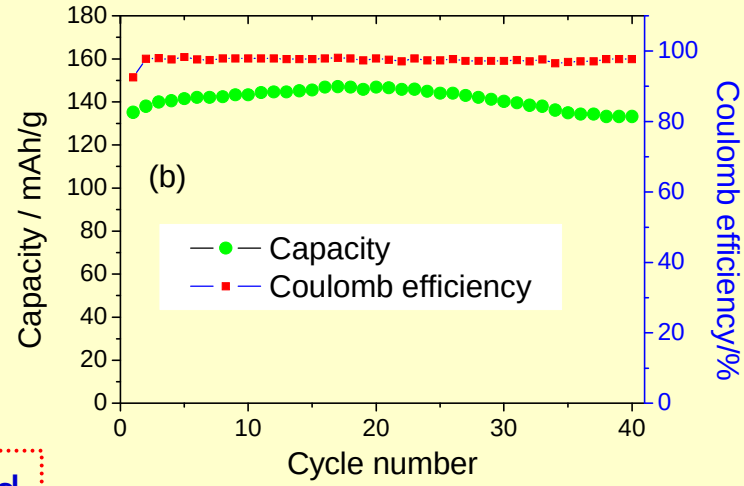




70C (less than 1'): (93%)

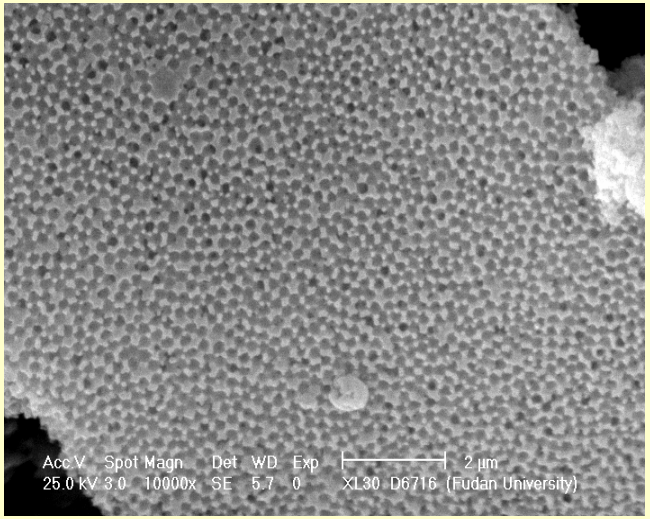
The fastest charge rate

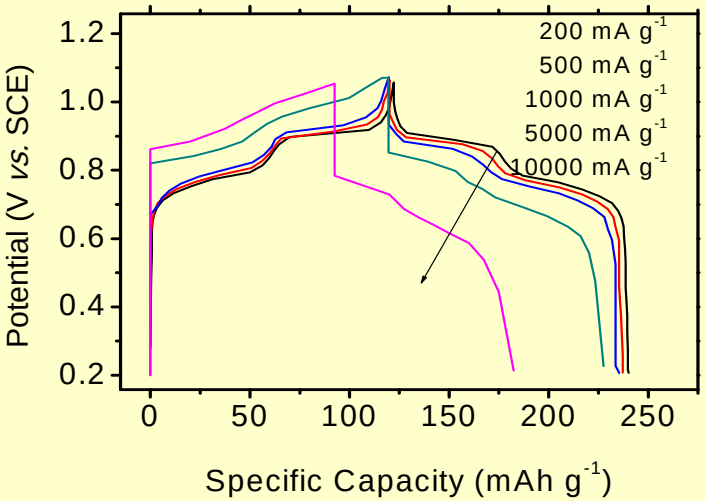
Promising for light HEVs.



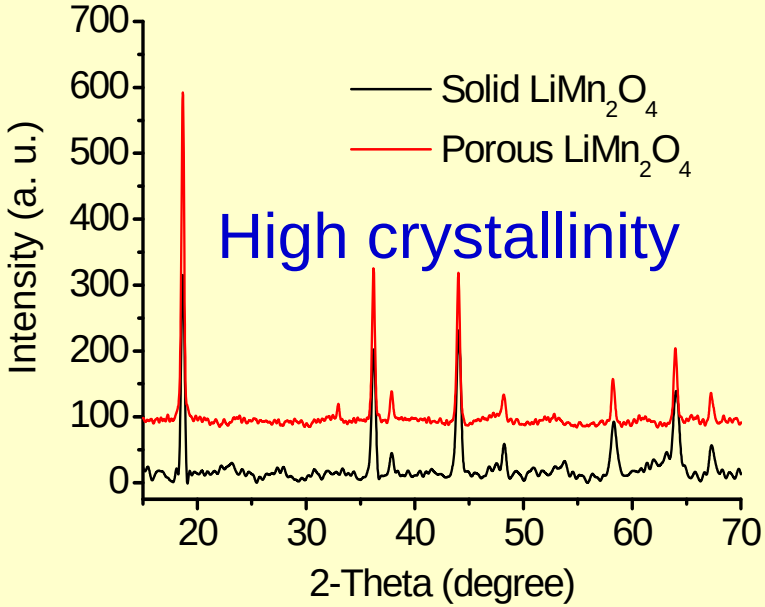
Wu et al., *Electrochem. Commun.*, accepted

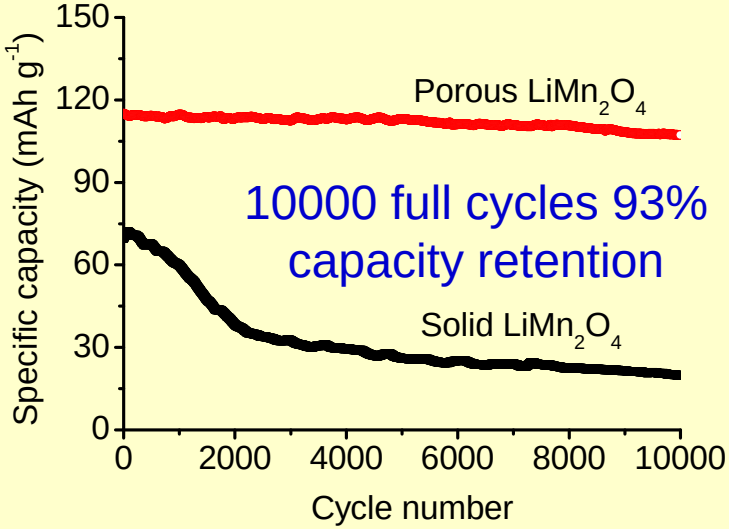
Porous $LiMn_2O_4$





Charge @90C, 76%: Excellent





Excellent cycle life: >30 yrs, lifetime maintenance-free

AC/K_2SO_4 solution/MnO_2 nanorods

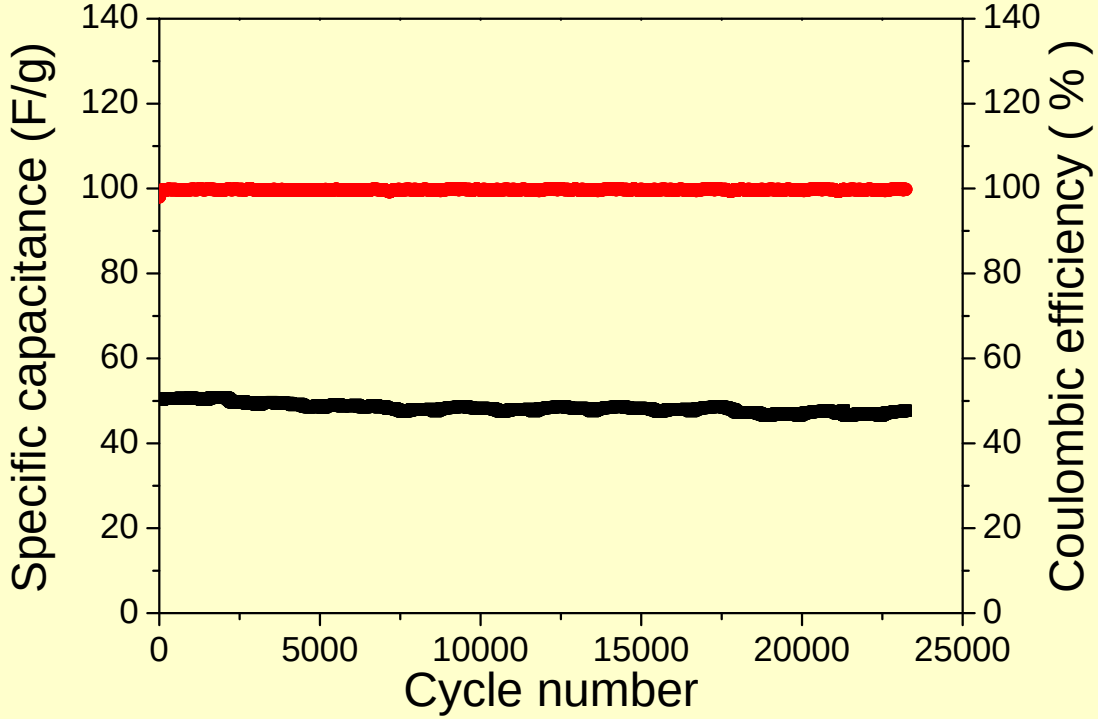
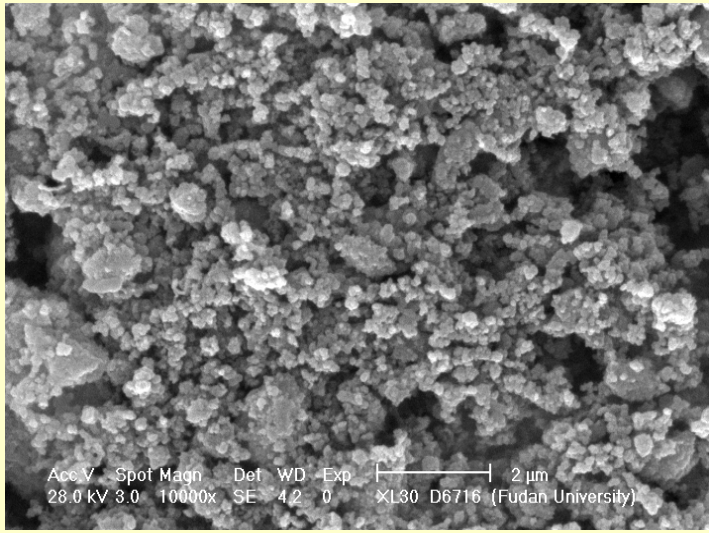
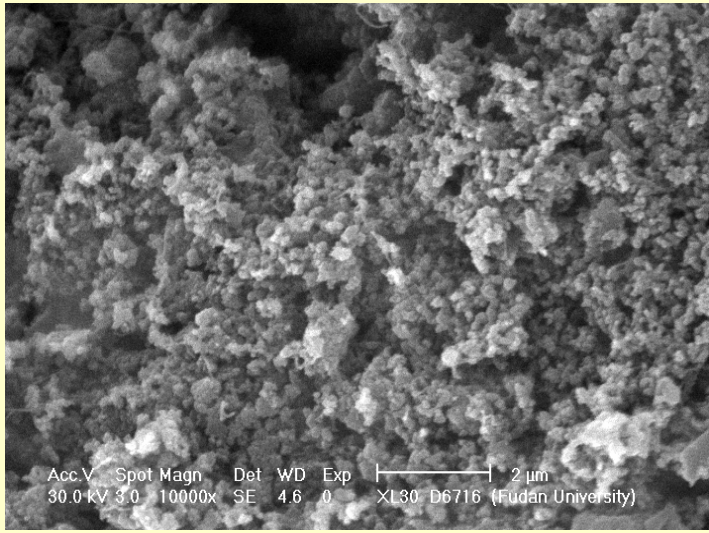


Fig. Cycling behavior of the supercapacitor AC/0.5 mol/l K_2SO_4/MnO_2 at a current rate of 10C between 0 and 1.8 V without removing oxygen.

Before cycles



After 23,000 cycles



Wu, et al. *J. Phys. Chem. C.* 113, 14020-14027 (2009).

AC//$LiMn_2O_4$

0-1.8V

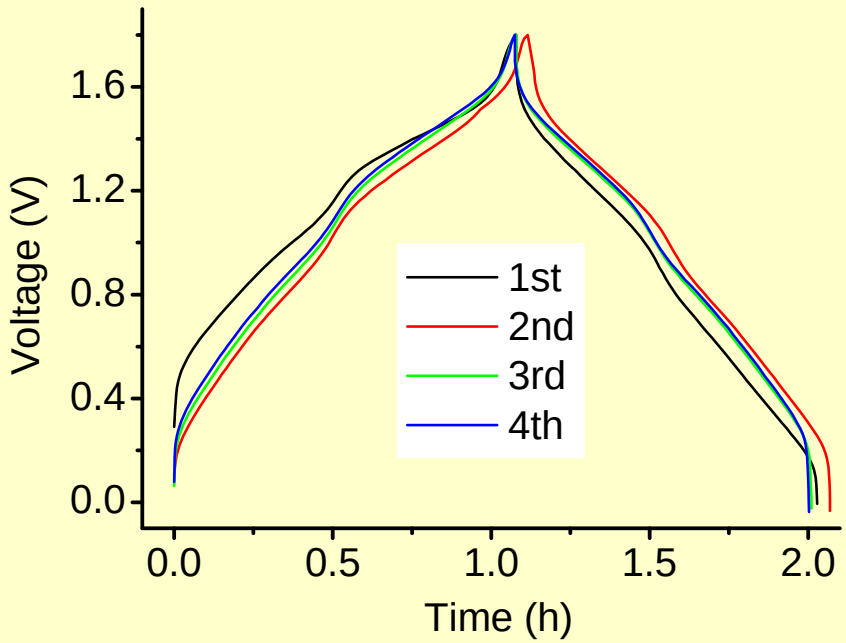


Fig. Charge and discharge curves of AC//Porous $LiMn_2O_4$.

>42 Wh/kg at low rate;

18 Wh/kg@2000 W/kg

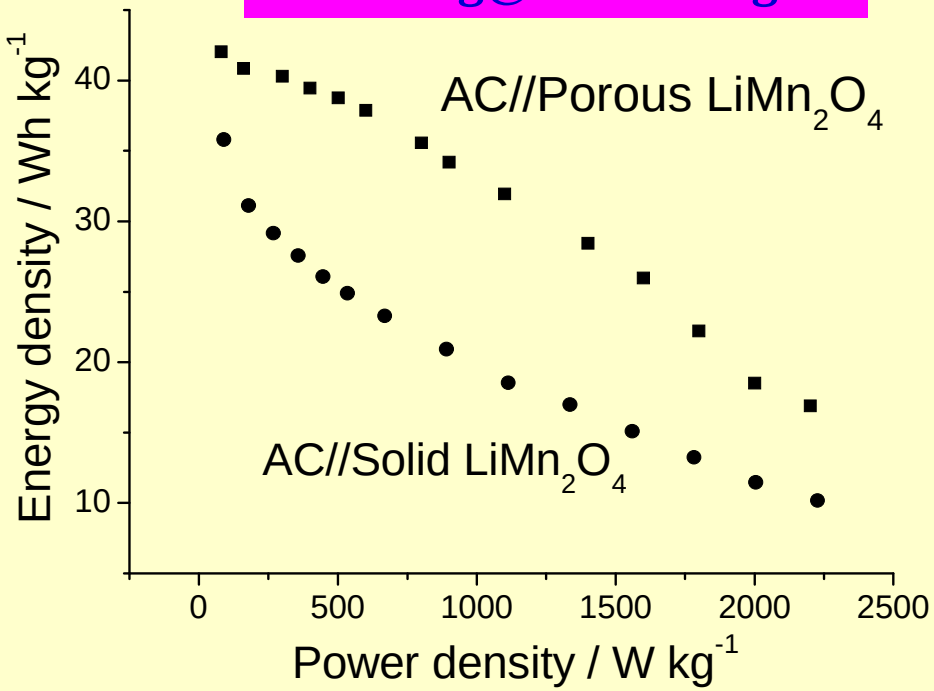


Fig. Ragone plots of AC//$LiMn_2O_4$ supercapacitor and symmetric AC//AC capacitor in 0.5 mol/l Li_2SO_4 aqueous solution.

AC//$Na_{0.27}MnO_2$

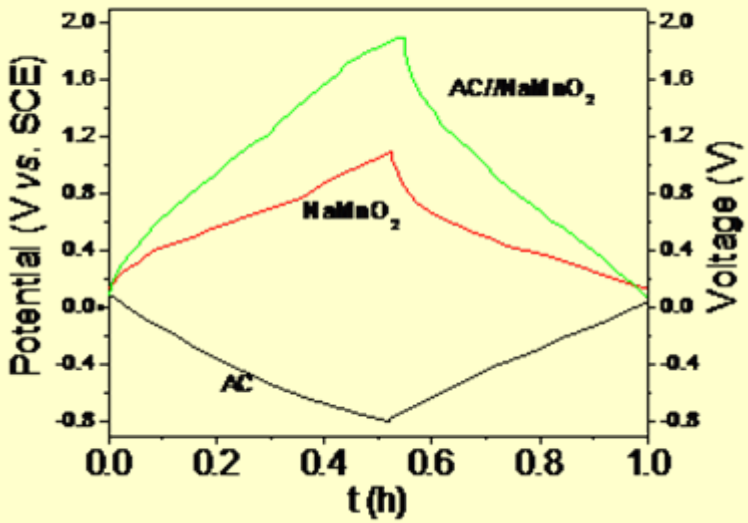


Fig. Potential-time curves of the individual electrode *vs*. SCE reference electrode and the voltage-time profile of the asymmetric AC//$Na_{0.27}MnO_2$ supercapacitor at a current rate of 2C in 0.5 mol/l Na_2SO_4 aqueous solution.

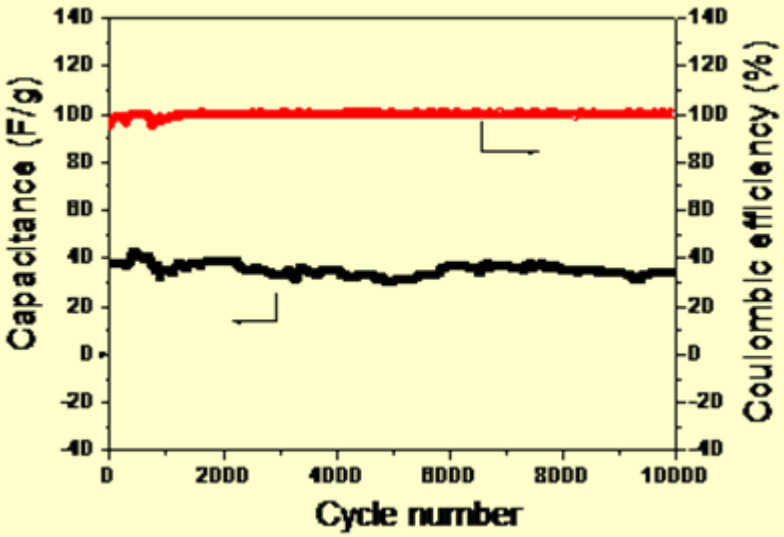
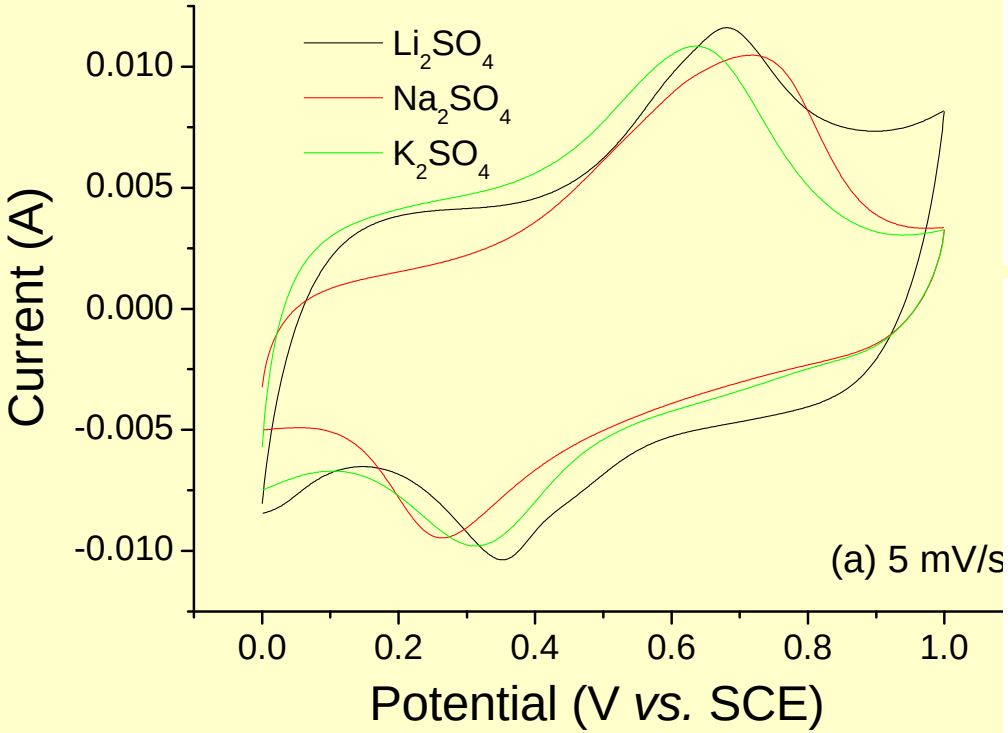


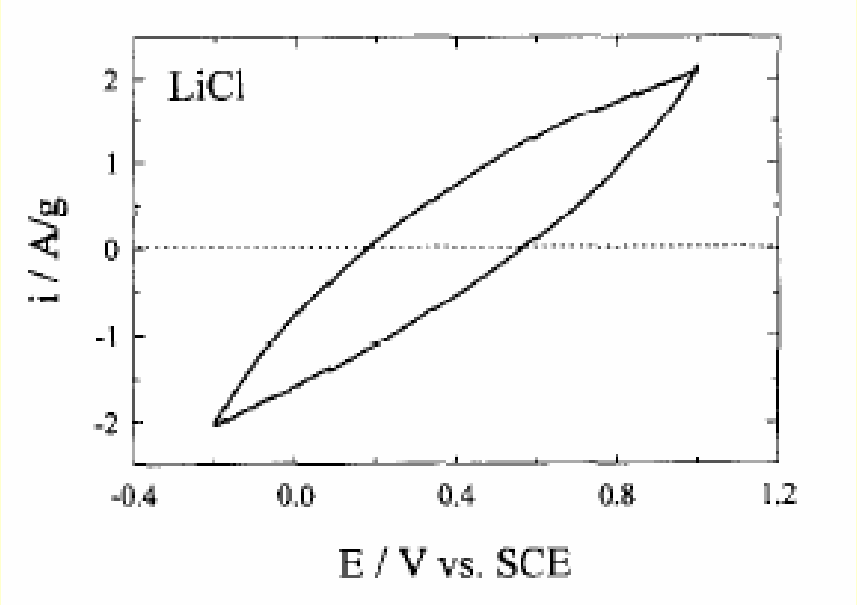
Fig. Cycling behavior of the asymmetric AC//$Na_{0.27}MnO_2$ supercapacitor at a current rate of 10C between 0 and 1.9V.

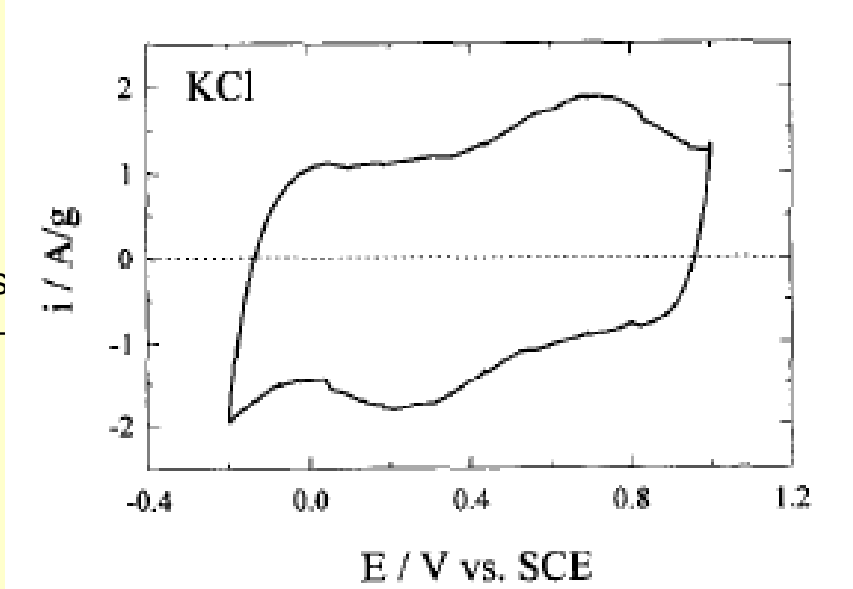
Patent pending.

AC//$K_{0.27}MnO_2$

Much better than formerly reported.



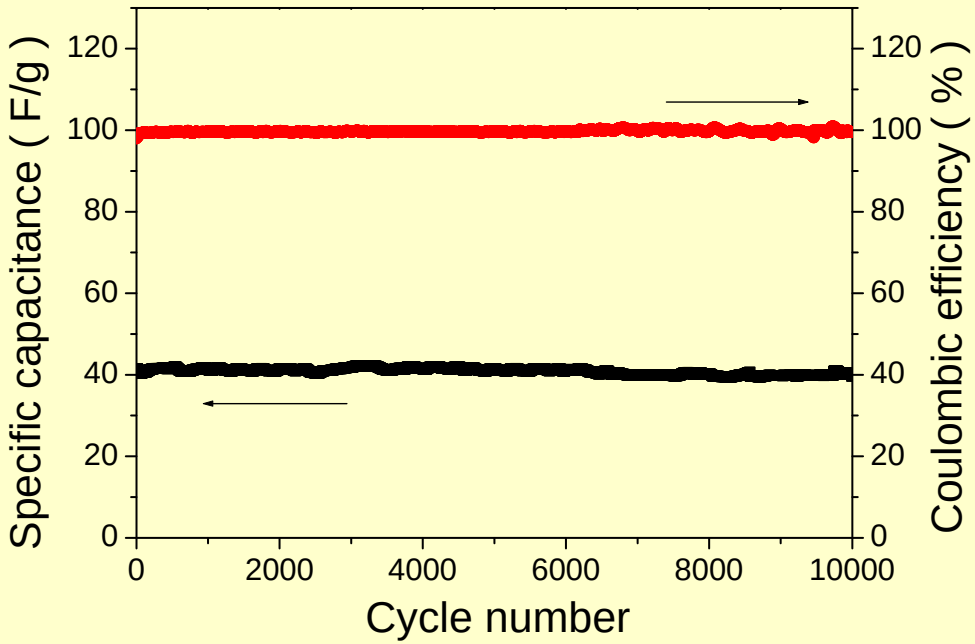




K_xMnO_2 in different solutions

J. B. Goodenough *et al.*

Excellent cycling & High energy density



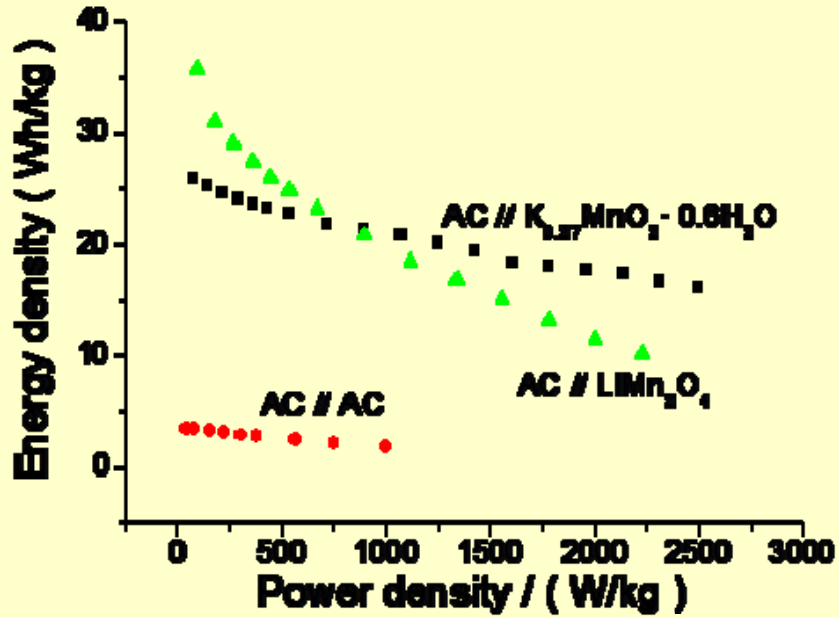
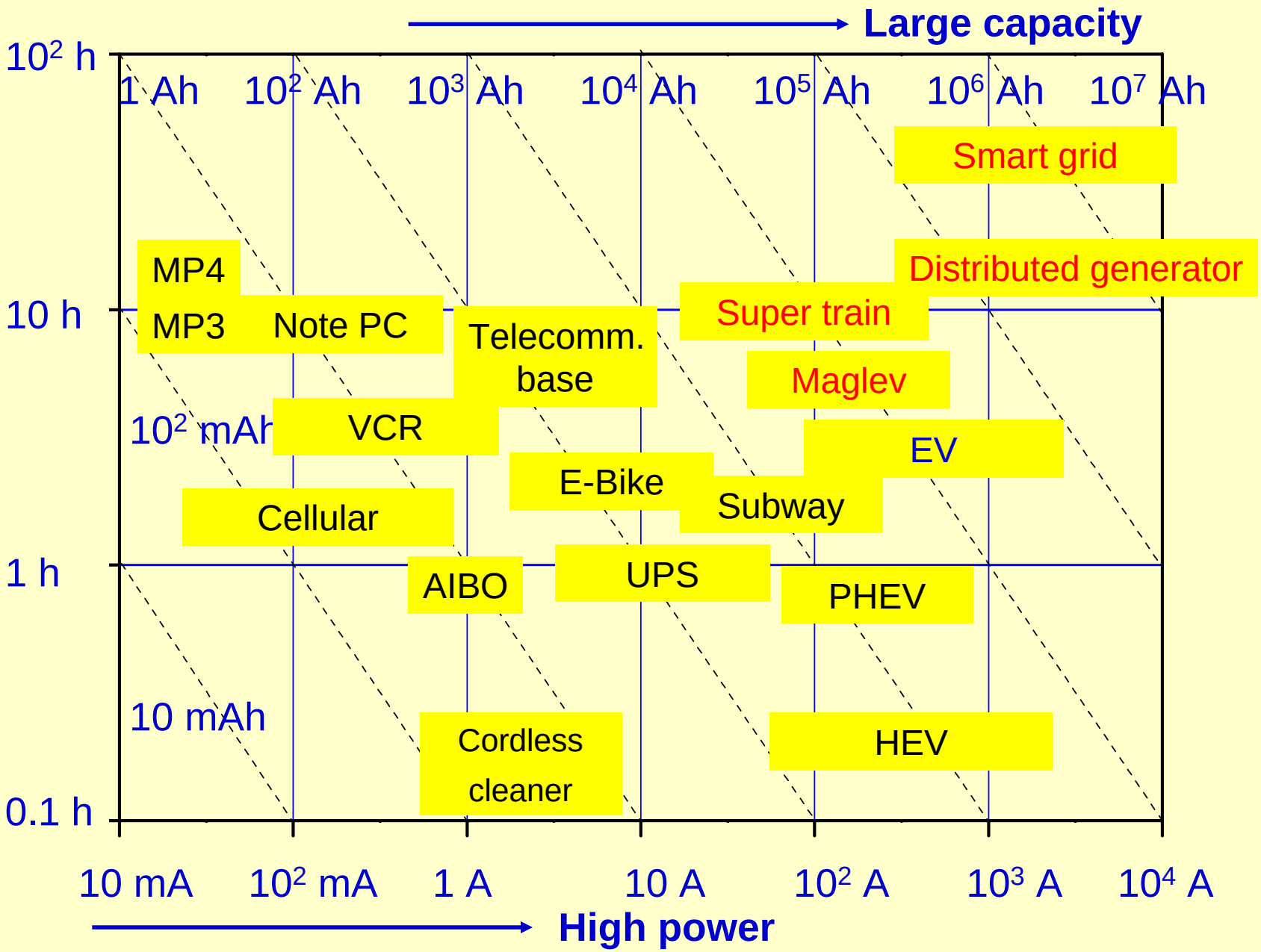


Fig. Cycling behavior of the supercapcitor AC//$K_{0.27}MnO_2$ between 0 and 1.8 V.

Fig. Capacitance variations of the $K_{0.27}MnO_2$•$0.6H_2O$ at different scan rates in 0.5 mol/l aqueous K_2SO_4 electrolytes.

Wu et al., *J. power. source*, 195, 2789 - 2794 (2010).

1. Applications of Lithium Batteries



Safety Problems

Recent recall announcement of LIBs

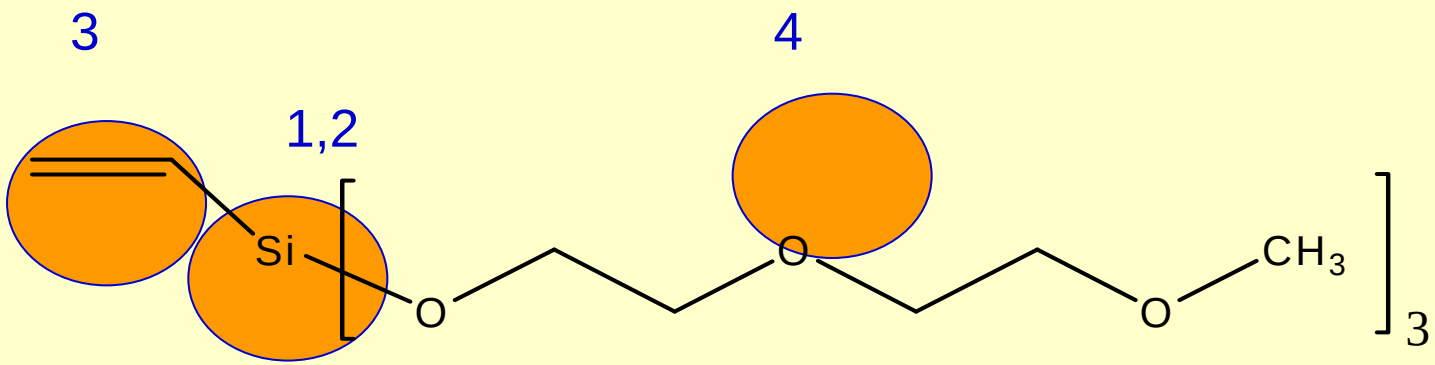
Date	Accident device	Recall scale
Aug. 2006	Sony cell in Dell note PC	4.1 M packs
Aug. 2006	Sony cell in Apple note PC	1.8 M packs
Oct. 2006	Sony cell in Toshiba & Fujitsu note PC	3.7 M packs
Dec. 2006	Sanyo cell in Mitsubishi cellular phone	1.3 M packs
Mar. 2007	Sanyo cell in Lenovo note PC	0.2 M packs
Jun. 2007	NEC-Tokin cell in Welcomm cellular phone	0.13 M packs
Jun. 2007	NEC-Tokin cell in KDDI cellular phone	0.07 M packs
Aug. 2007	Panasonic cell in Nokia cellular phone	46 M packs
Mar. 2008	NEC-Tokin cell in Kyocera cellular phone	0.21 M packs
Jun. 2008	Sony cell in note PC	0.438 M packs
Mar., 2010	HP note PC	-
Jul. 2010	Sony cell in note PC	0.055362M packs

These recall scales suggest the accident possibility is ppm order.

2. Flame Retardants

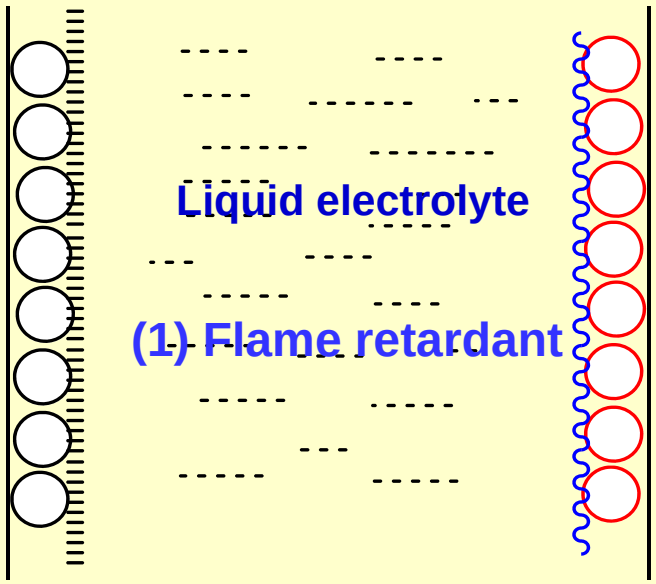
- Main problem for LIBs: Safety & Reliability
- Liquid electrolytes: Mixture of DEC, DMC and EMC
- Flame retardants: organo-phosphate, X-containing compounds and biphenylene
- Problems: harm & decrease of ionic conductivity

New flame retardant: Molecular design - VTMS



1. Si-O bond: flame retardant, ionic conductor
2. Si-O bond: form a surface layer on cathode and reduce the direct contact area between cathode and electrolyte
3. Double bondage: participate the formation of SEI film on anode materials like VC
4. $–CH_2-CH_2-O-$: ionic conductor

New Reaction Mechanism



(3) Participate the formation of SEI film and prevent the direct contact of Li_xC_6 and electrolyte

(2) Form a protective film on the cathode and reduce the direct contact area between cathode and electrolyte

(1) + (2) + (3) → **Ameliorate the safety**

(1) + (4) → **Ensure good electrochemical performance**

→ **Applications**

Patented.

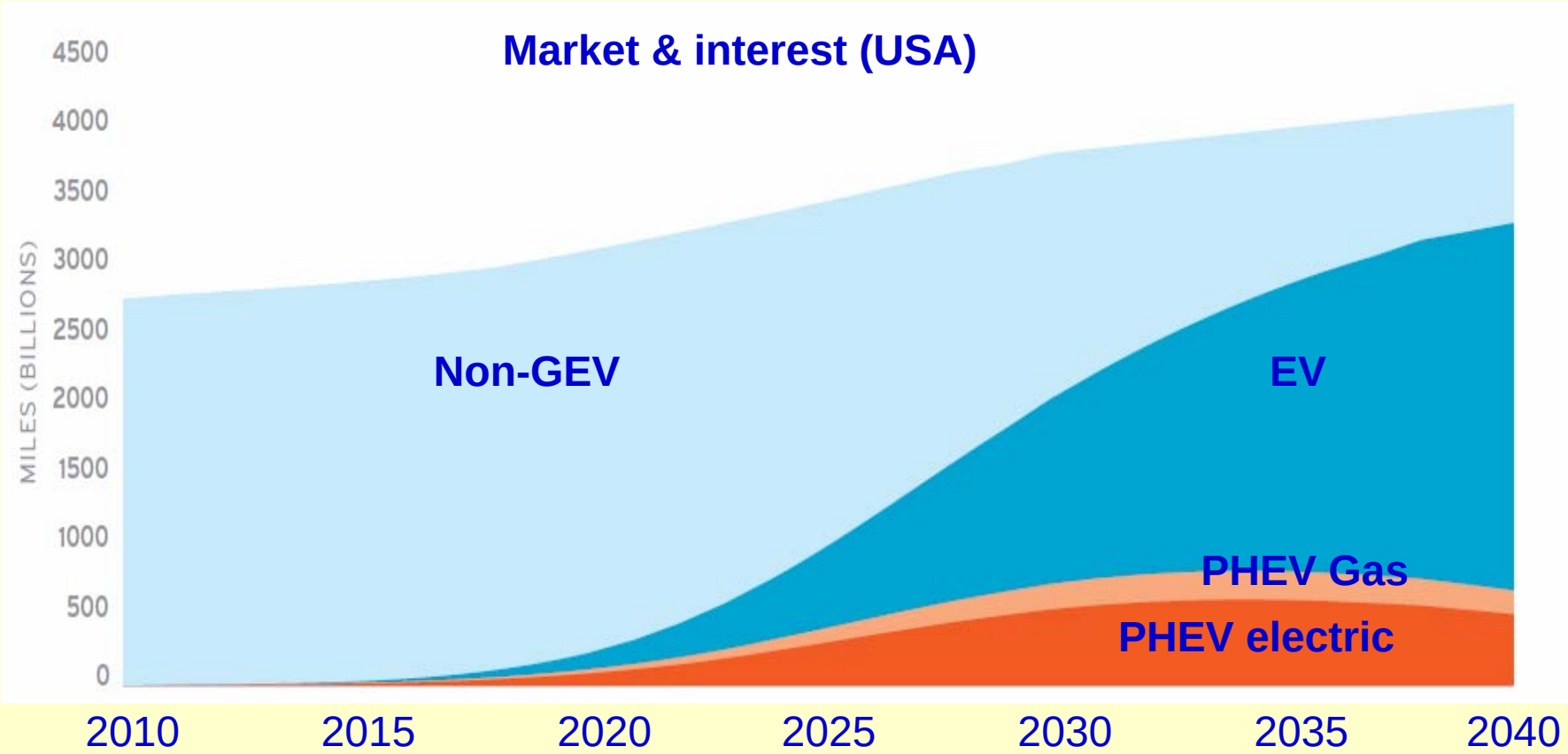
Wu et al., *J. Power Sources*, 180, 602 (2008)

3. Gel Membranes (GMs)

note PC: 40 Wh (=5 Ah x 8V) → iMiEV: 16000 Wh (= 50 Ah x 330 V)

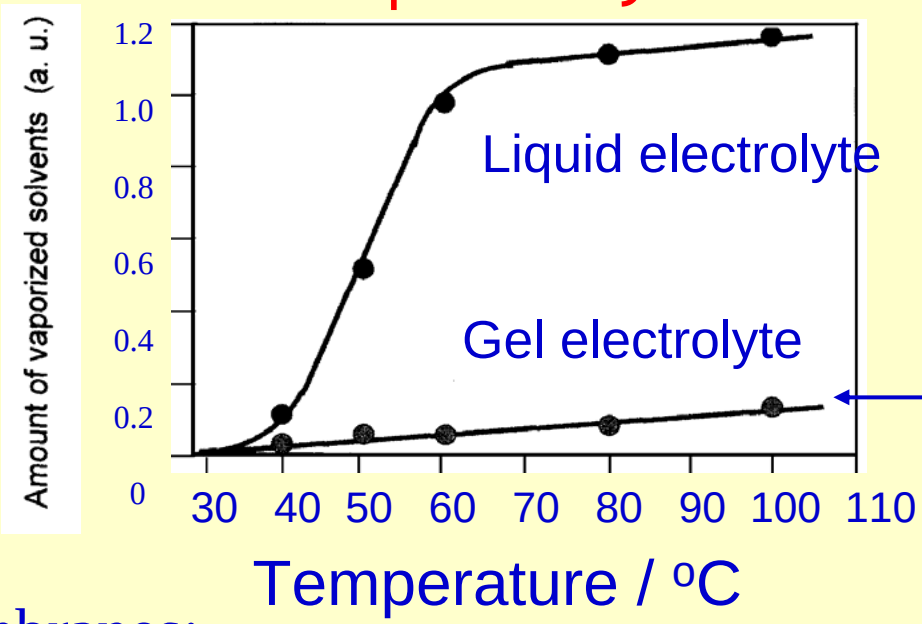
Accident risk is in proportion to the square of the total cell energy.

A lot of fire reports for HEV, PHEV and EV.



What will be the next step ?

Safety → { Anode, Cathode, Electrolyte, Separator } → Gel electrolytes



Separator

Electrolyte + gel membrane

Reactions of anode and cathode with the electrolytes will be greatly decreased.

First choice for LIBs of HEVs and EVs.

Gel membranes:

- Good safety
- High ionic conductivity
- Good surface performance with electrodes.

- GMs: based on PEO, PAN, PMMA, PVDF, P(VDF-HFP)…

Main factors:

- **Porous structure**
- **Mechanical strength**
- **Processing performance**

} Contradicting

Bellcore Company: sold its technology to 23 companies over the world, and on success ?

Manufacturing methods:

(a) Phase inversion

Low efficiency, low qualification, and high cost.

(b) non-solvent induced phase separation technique

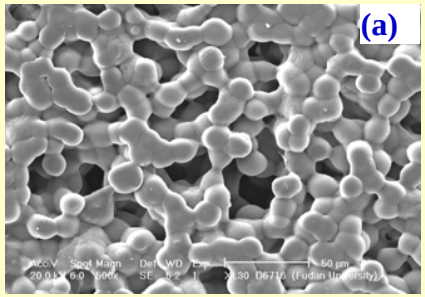
- Wet: Exchanging the non-solvent with solvent (easily shrink, poor mechanical performance)
- **Dry: Removing non-solvents by drying at elevated temperature (dimensionally stable)**

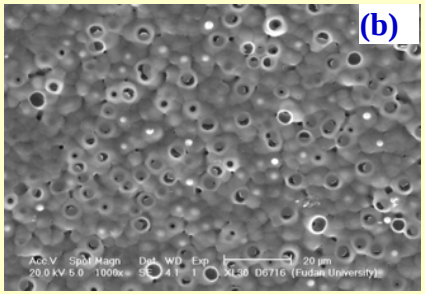
(1) *In situ* adding nano fillers to improve the dispersion and mechanical strength.

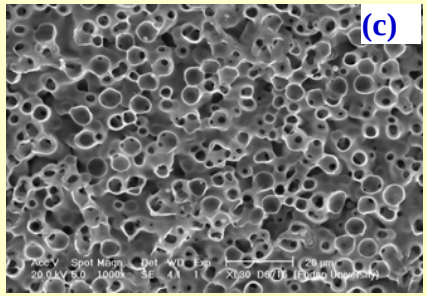
(2) Changing the non-solvent to control the morphology of the polymer membrane.

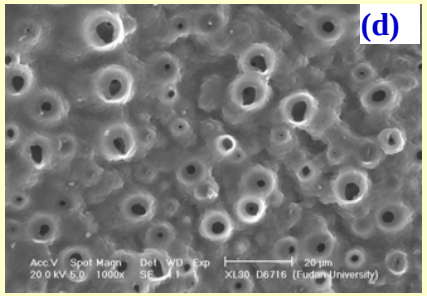
SEM micrographs of the partial prepared gel membranes containing different amounts of TiO_2.

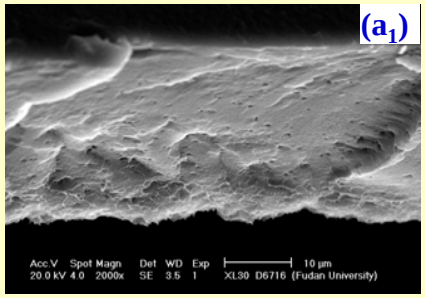
Surface: (a) 0 wt.%, (b) 5.1 wt.%, (c) 9.0 wt.%, (d) 14.0 wt.%

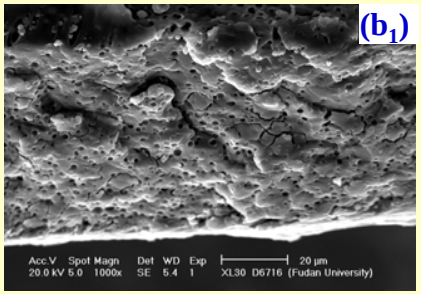


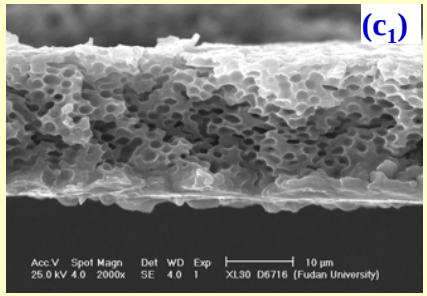


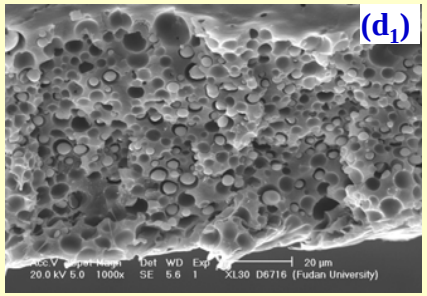






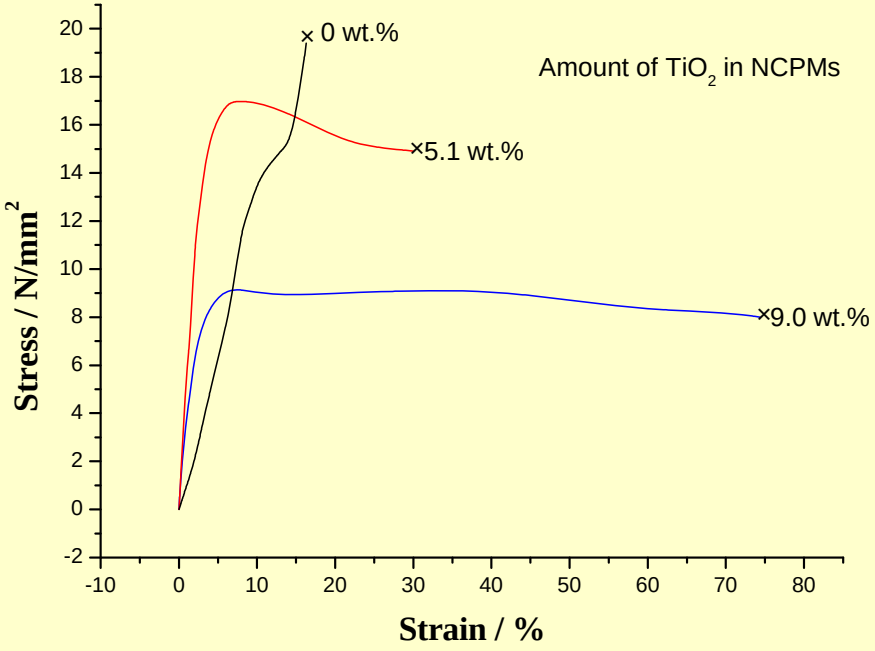


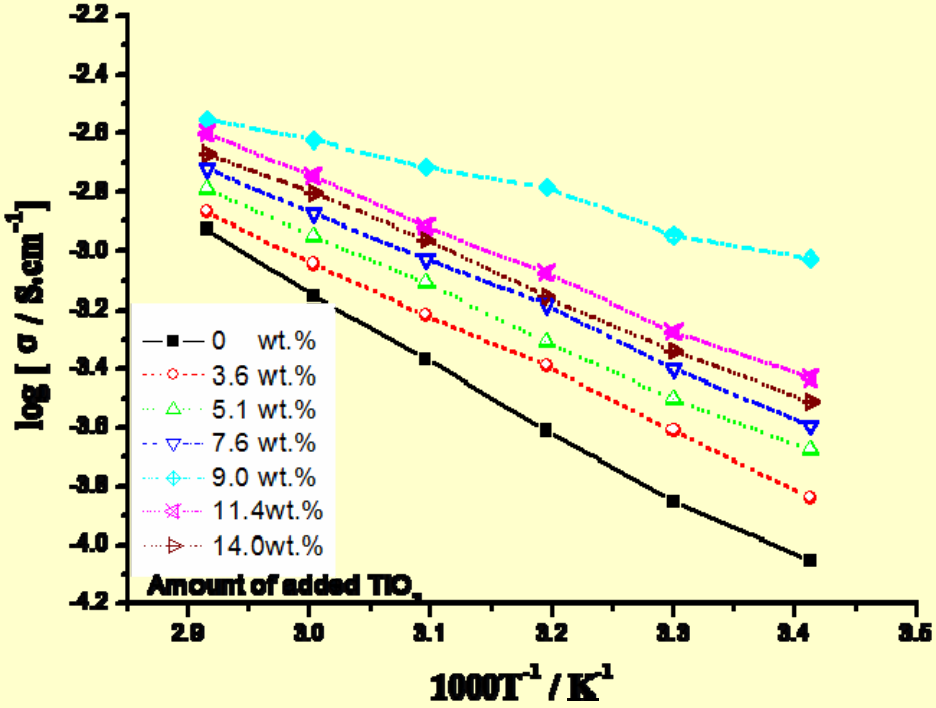




Cross-section:

(a_1) 0 wt.%, (b_1) 5.1 wt.%, (c_1) 9.0 wt.%, (d_1) 14.0 wt.%



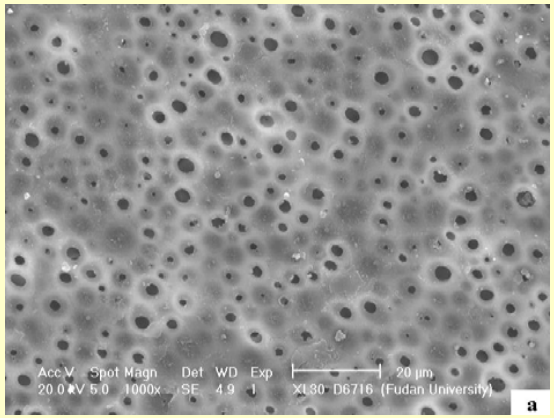


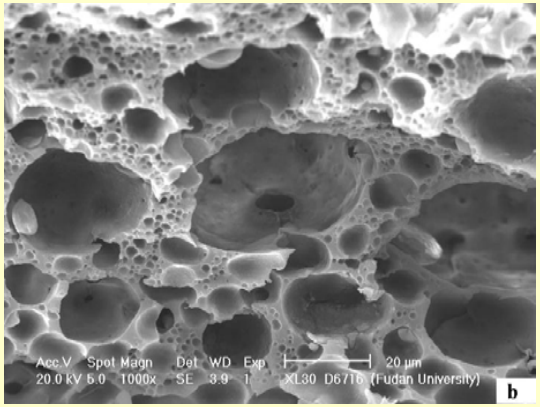
Stress-strain curves for some gel membranes.

log σ ~1/T curves for the prepared gel electrolytes.

Lotus root-like GMs

Preparation process: P(VDF-HFP) + glycerol + NMP@ pH = 1.0. → + $Ti(OC_4H_9)_4$ + H_2O → cast on a clean glass plate@ 80°C for 6 hrs → self-supporting polymer membrane → immersing in a water bath at 80°C for 2 hrs → drying under vacuum at 100 ^{o}C overnight → a lotus root-like porous nanocomposite polymer membrane.

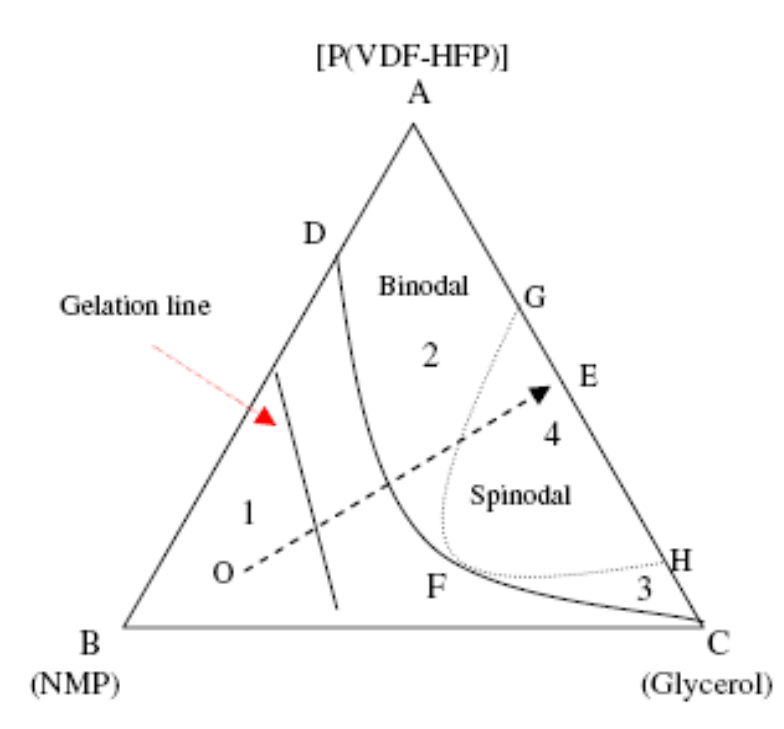


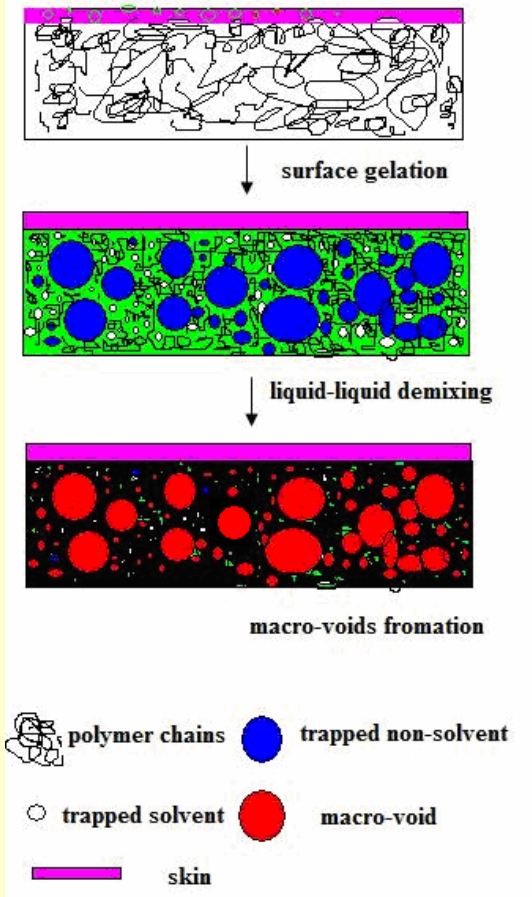


NMP: 203 ^{o}C
Glycerol:
bp. 290°C

(a) Surface and (b) cross-section morphologies of the porous nanocomposite polymer membrane.

Formation mechanism





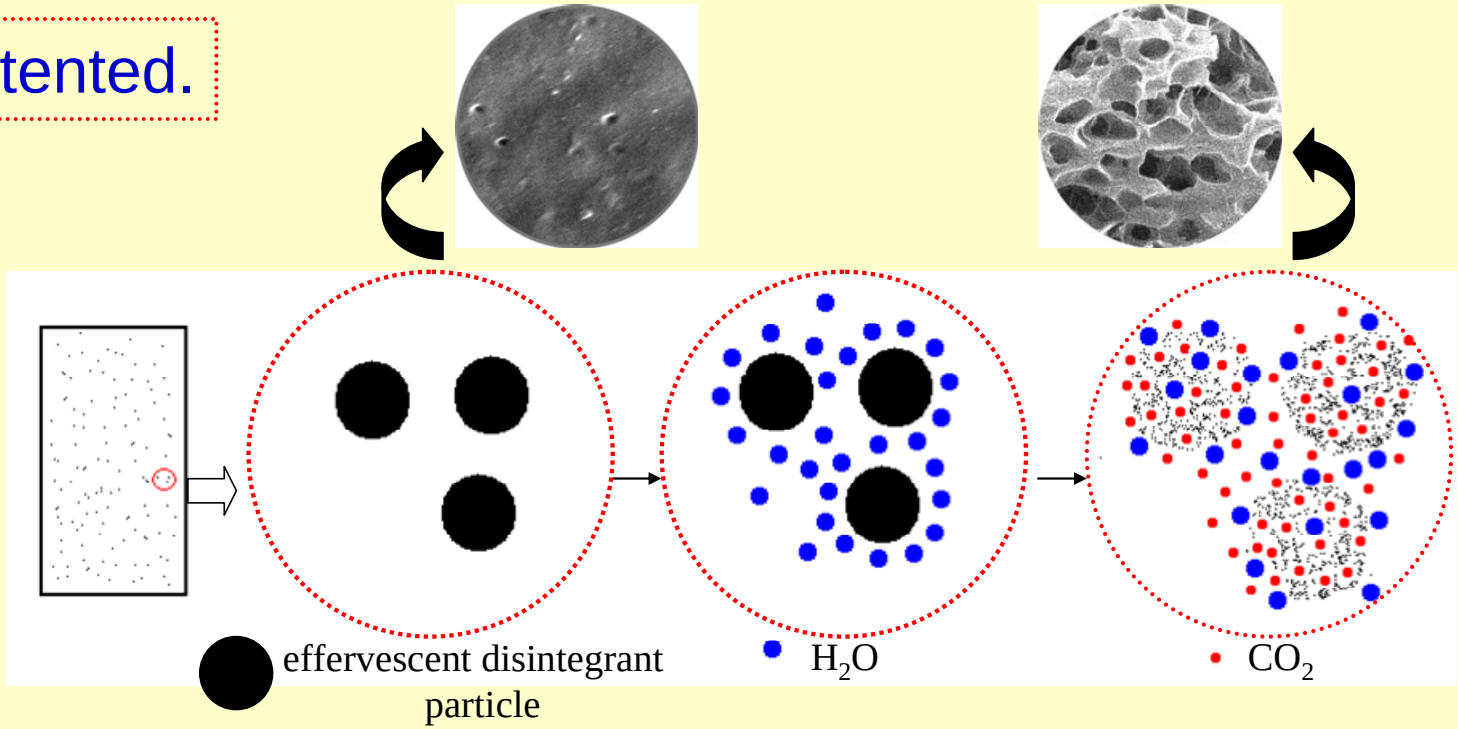
TiO_2: interface stabilizer
polymer-poor phase: macropore
polymer-rich phase: micropore

Qualitative ternary phase diagram of P(VDF-HFP) / NMP / glycerol (left) and the sketch of the formation of the porous polymer membrane (right).

Other Methods to Prepare Gel Membranes

Microwave-assisted foaming process

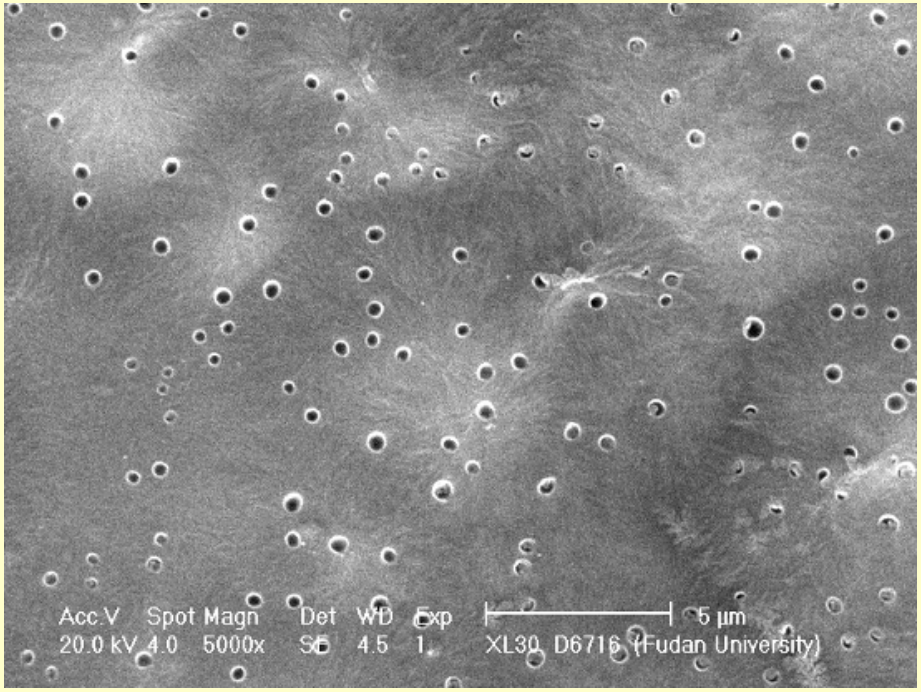
Patented.

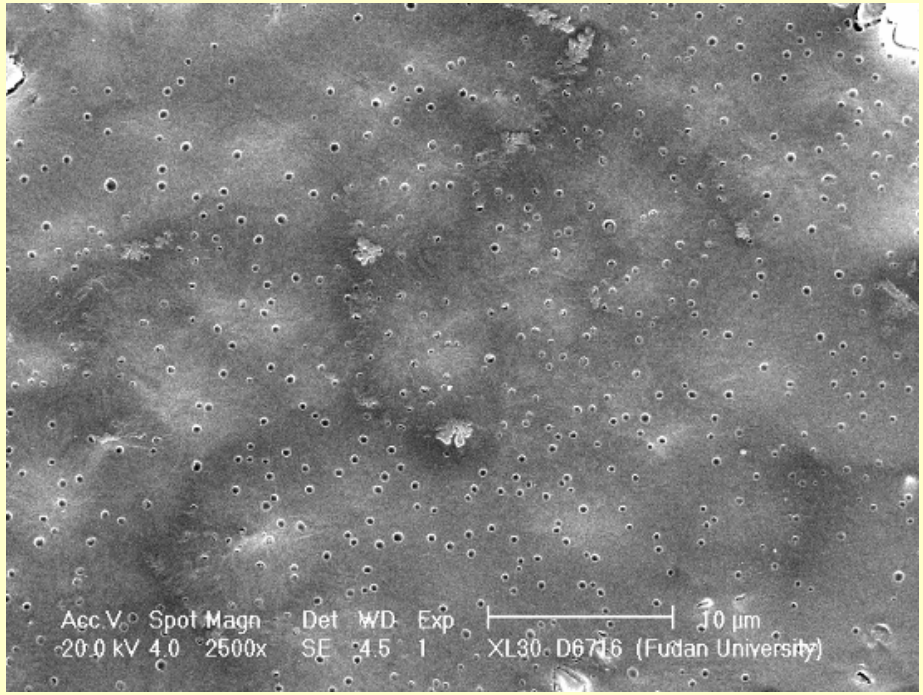


The schematic process to prepare porous polymer membrane by a microwave assisted effervescent disintegrable reaction.

Wu et al., *J. Memb. Sci.*, 362, 113-118 (2010)

Salicylic acid as a foaming agent





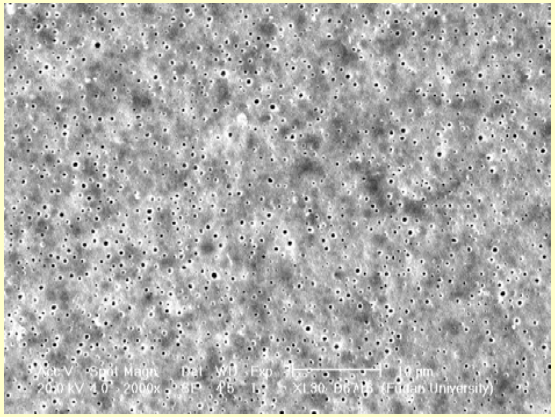
Porous PVDF

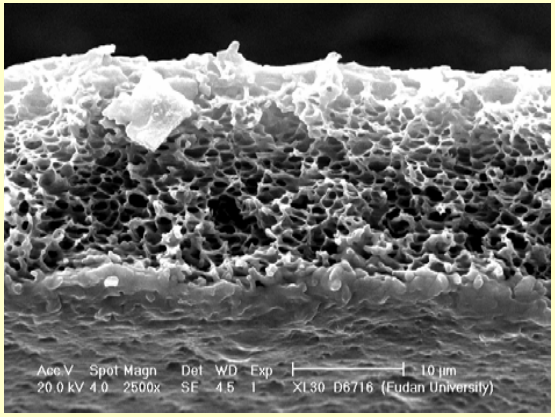
Wu et al., *Electrochim. Acta*, 54, 4403 (2009)

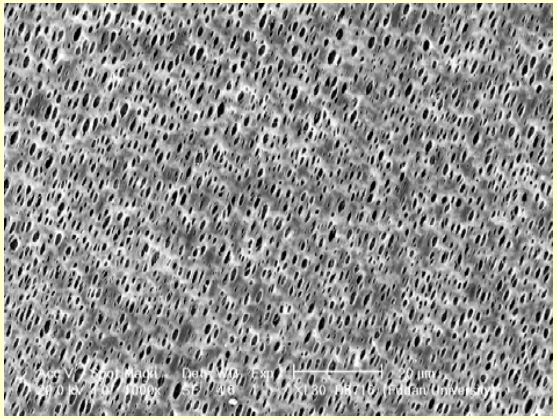
Further Modification of Gel Membranes

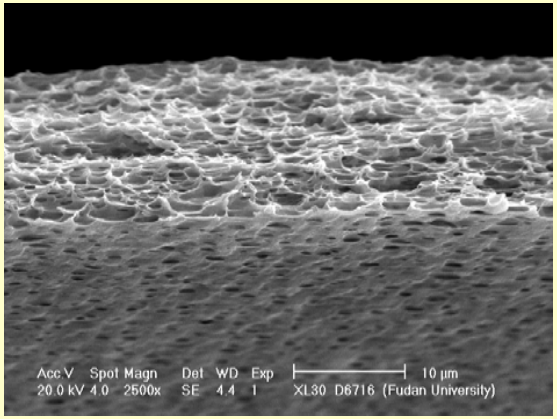
Original

Stretched









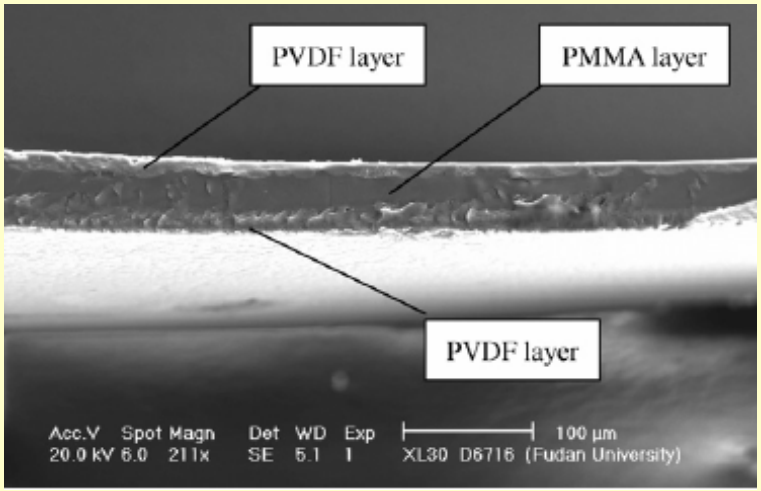
Bottom surface

Cross-section

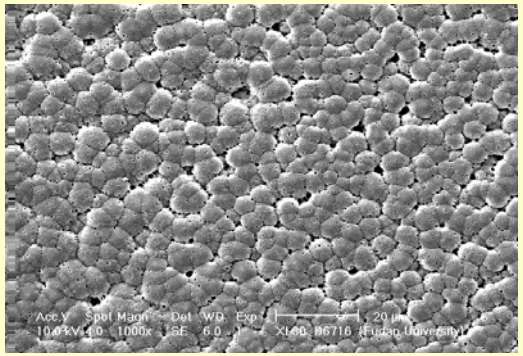
Wu et al., unpublished

Patented.

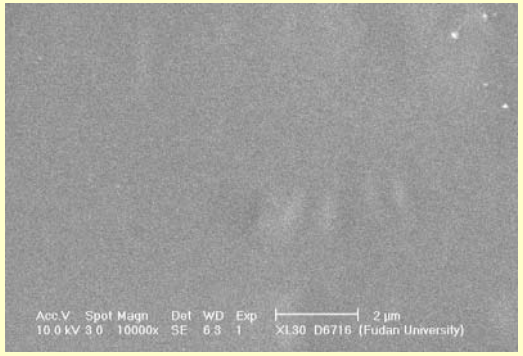
Sandwiched GM



SEM micrograph of the cross-section of the sandwiched membrane of PVDF/PMMA/PVDF.

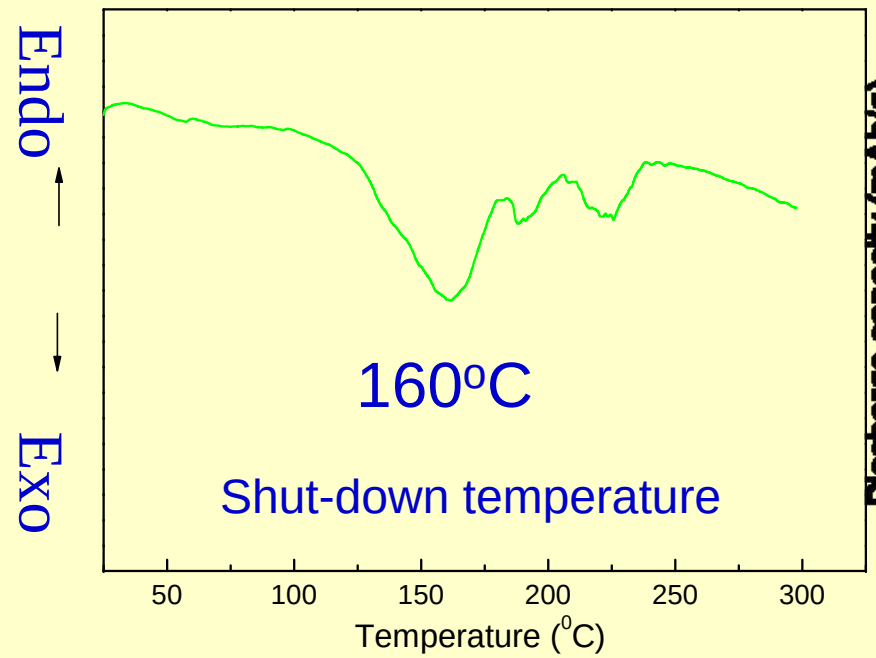


(a)



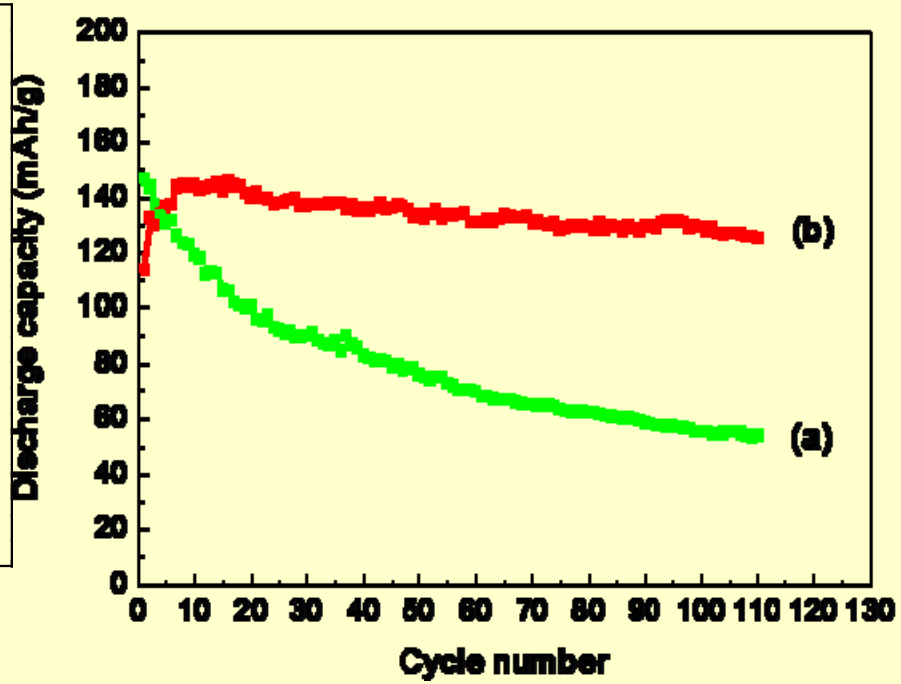
(b)

SEM micrographs of the surfaces of (a) the outer PVDF layers and (b) the inner PMMA layer in the sandwiched PVDF/PMMA/PVDF.



DTA curves of GEs based on the sandwiched PVDF/PMMA/PVDF membrane.

Wu et al., *Electrochem. Commun.*, 9, 1700 (2007).



Cycling performance of (a) Li/Celgard 2400 + liquid electrolyte/$LiCoO_2$ and (b) Li / sandwiched PVDF/PMMA/PVDF membrane + liquid electrolyte /$LiCoO_2$ between 4.4 and 3.0 V.

Our Lab’s Capability to Manufacture LIBs

Weighing

Mixing

Coating

Cutting

Rolling

Point welding

Ultrasonic welding

Winding

Laser welding

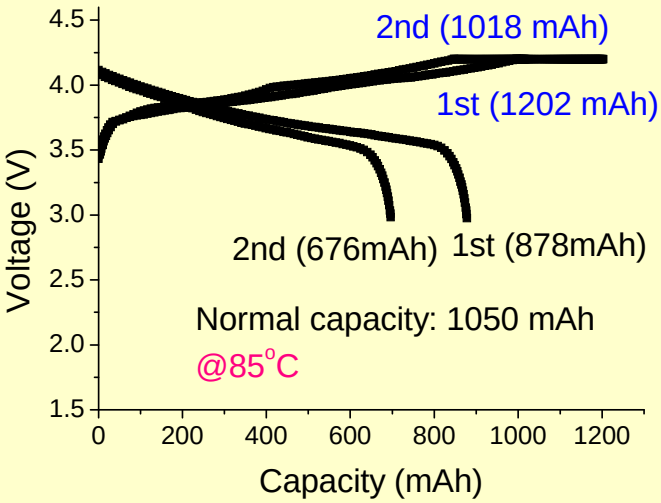
Electrolyte Filling

Forming

Testing (0.0001-50A)

Our First GMs

Graphite/GM/$LiCoO_2$



Before cycling

after 2 cycle@85°C

2 cycles: total time 6 hr and 9 mins
Thickness: from 6.3 mm to 7.5 mm
Storage: full charge @85°C 12hr, very little size change.

Full charge and then put on electric oven:

1 min and 10 seconds: safety time to escape when EVs are on fire.

Wu et al., unpublished

Analysis Results

Cap

Case

Pellet

- Copper: left Endothermal
- Aluminum: oxidized Exothermal
- Electrolyte: burned Exothermal
- Anode: burned Exothermal
- Cathode: oxidized Exothermal
- GM (PVDF): burned Exothermal

Safety greatly improved!

Safety: priority!!!

Advantages & disadvantages of our GMs

	Separators	GMs of Japan & South Korea	Our GMs
Main components	PE, PP	PE, PP, PMMA	PVDF
Demands on equipments	Very high	Very high	Fair
Manuf. process	Simple	Complicated	Simple
Non-combustibility	Poor	Poor	Very good
High temp.	60°C	85°C	85°C
Safety	Fair	High	Very high
Ionic conduc.	Very good	Good	Good
Cycling behavior	Good	Very good	Very good
Creep behavior	**Poor**	**Poor**	**Good**
Long-term safety	**Poor**	**Poor**	**Good**

Twice Study Tours to Shanghai Expo (2010) for our NEML

Acknowledgment

Financial sponsors

- National Basic Research Program of China (973 Program No: 2007CB209702)
- Natural Science Foundation Committee of China (**One first project on ARLBs in China**)
- Ministry of Science and Technology of China
- Science and Technology Commission of Shanghai Municipality
- Alexander von Humboldt Foundation (Partership Program)
- Sanyo Chemical

Thank you very much for your kind attention !