动力锂电池及其挑战性问题

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Motto of NEML

4E + E

Electrochemical technologies

Solve

Reduce

Energy problems

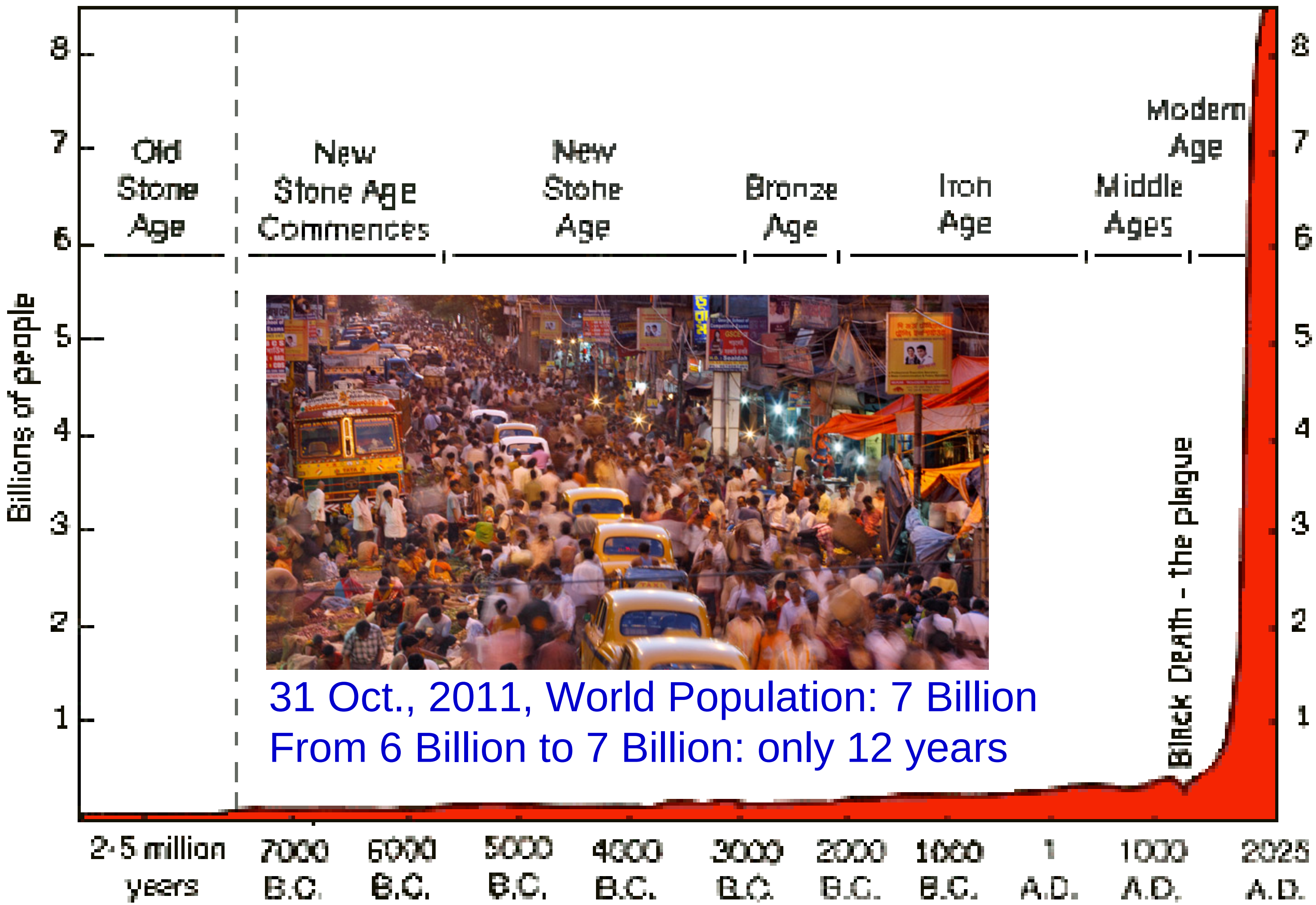
Environmental pollution

Enjoy life

To cultivate **E**lites for the society.

1. Introduction

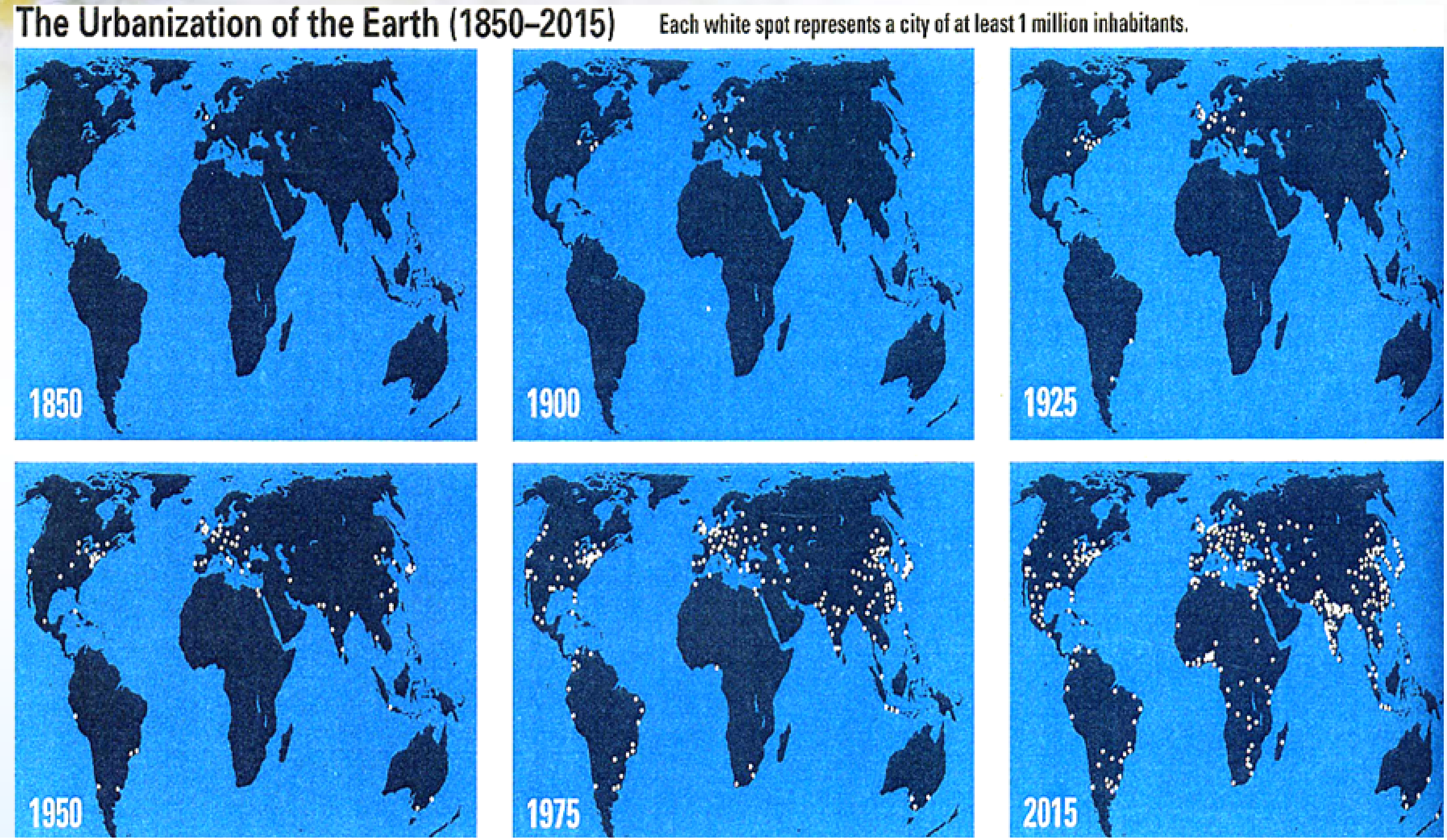
World Population Growth Through History



31 Oct., 2011, World Population: 7 Billion

From 6 Billion to 7 Billion: only 12 years

Urbanization



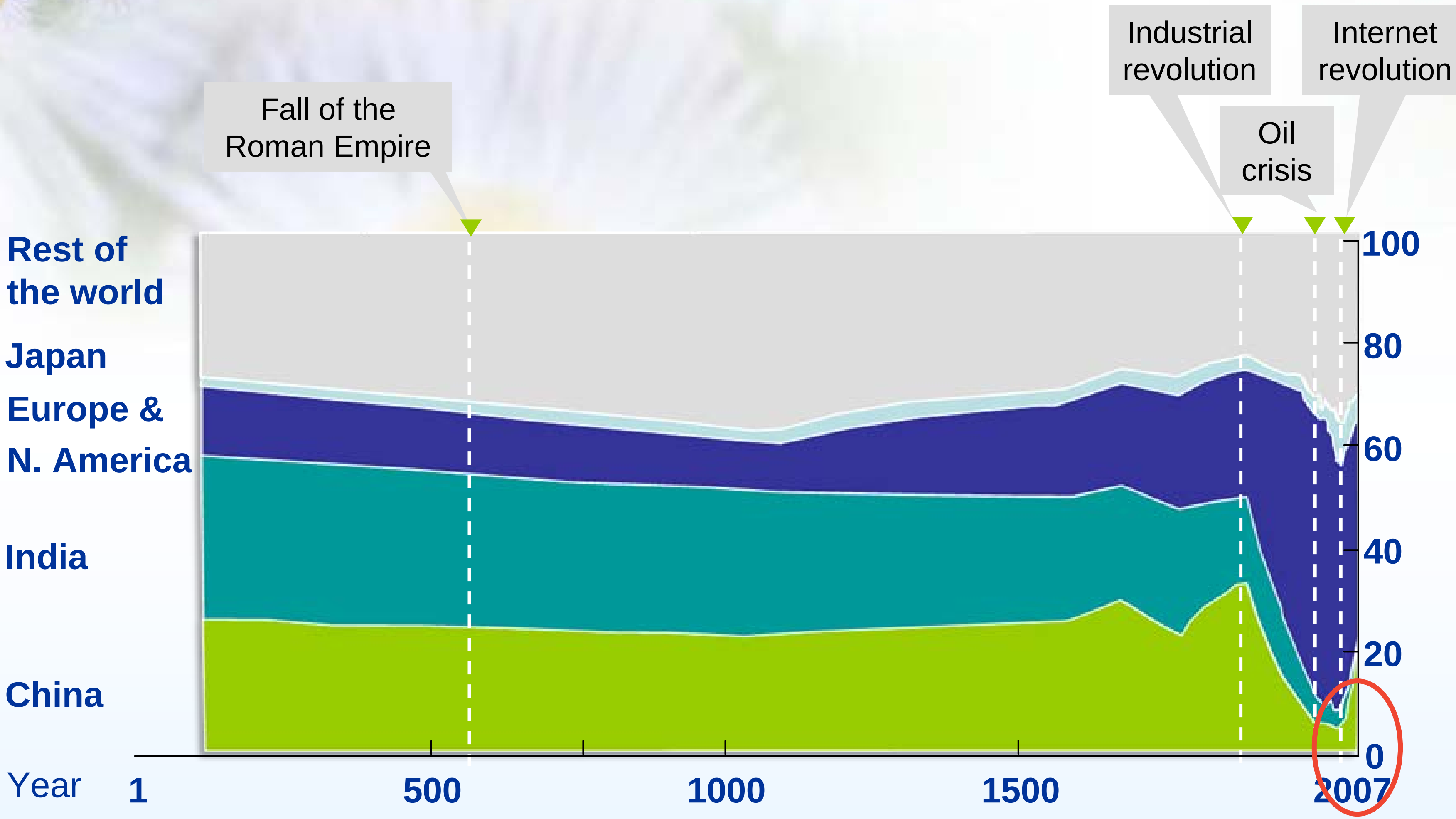
Urbanization: Half the world population now lives in urban areas

25 cities with over 10 million population;

300 cities with over a million population

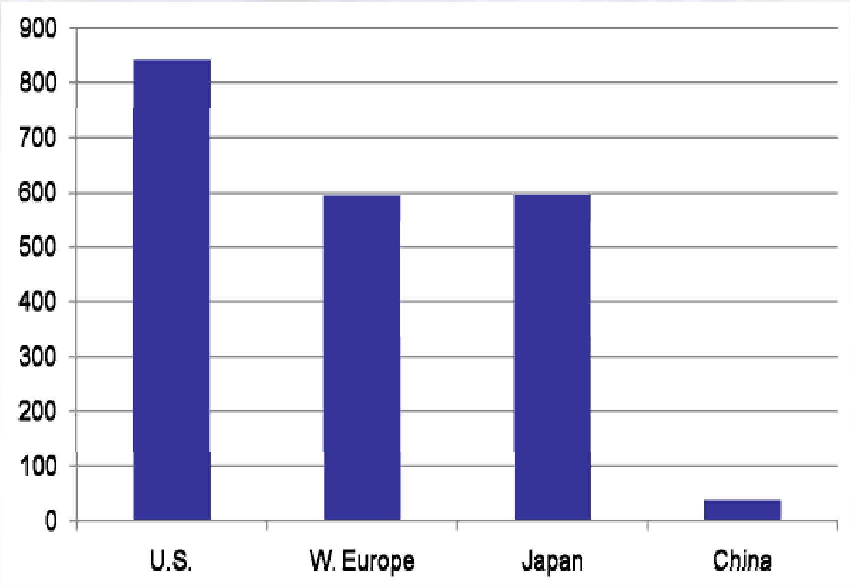
Source: Philips University Atlas

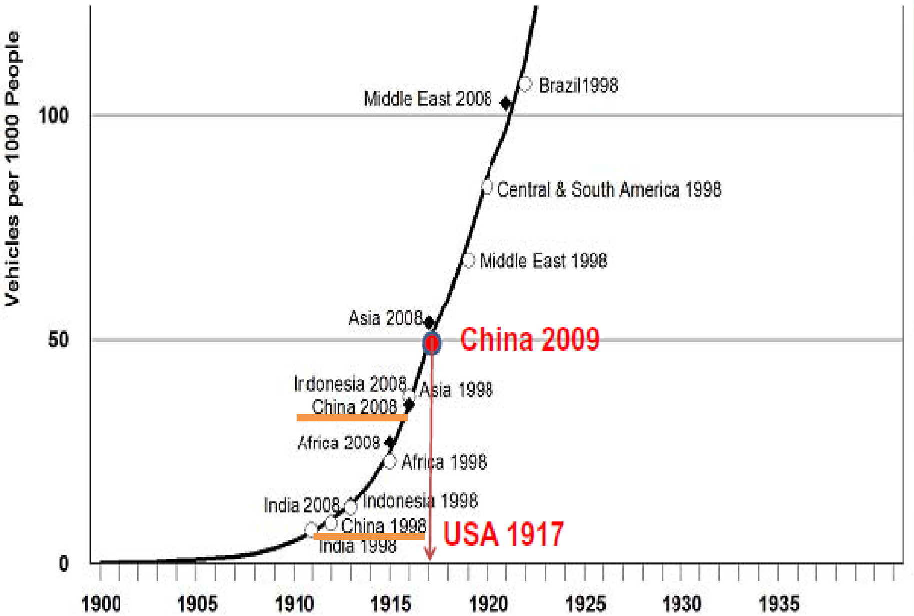
Changing Composition of World GDP



***Source**: Angus Madison's 'Historical Statistics for the World Economy: 1-2004 AD', Deutsche Bank Global Market Research. Courtesy Pedro Rodeia, McKinsey*

China *vs* USA

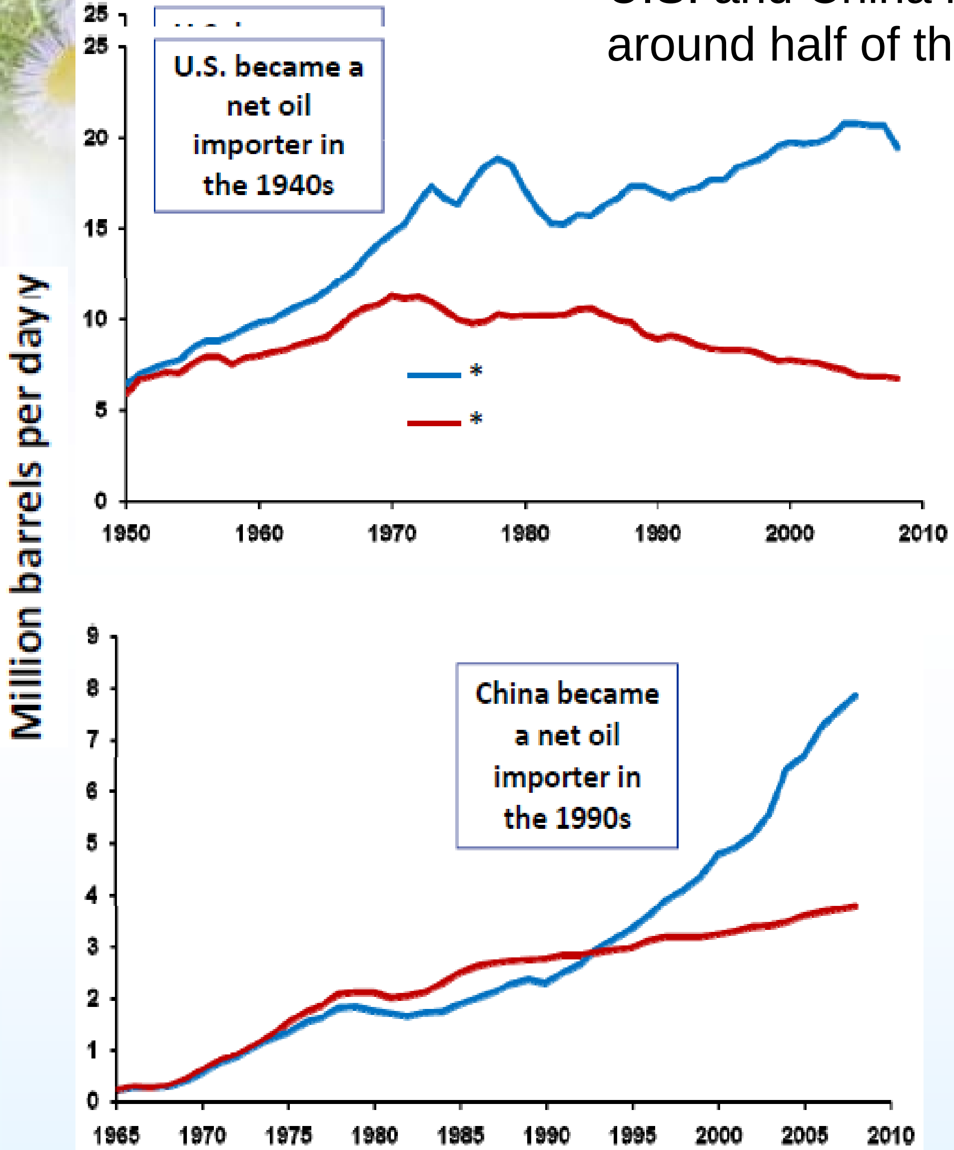


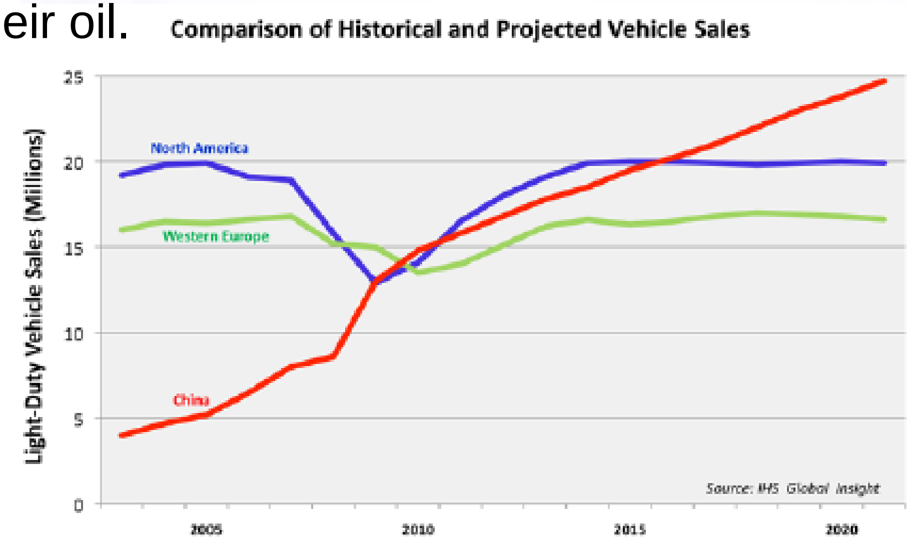


- China enters the rapid increasing period from 1998 (USA after 1912)
- China took 10 yrs (1998-2009) *vs* USA 15 yrs (1912-1917) for same vehicles per 1K people increased
- China is about 90 years late just from the amount of vehicles per 1K people

  - Source: Tsinghua Uni. and US DOE

U.S. and China import around half of their oil.





- Source: US DOE and IHS Global Insight

Advantages of Electric vehicles

- Energy crisis
- Energy efficiency

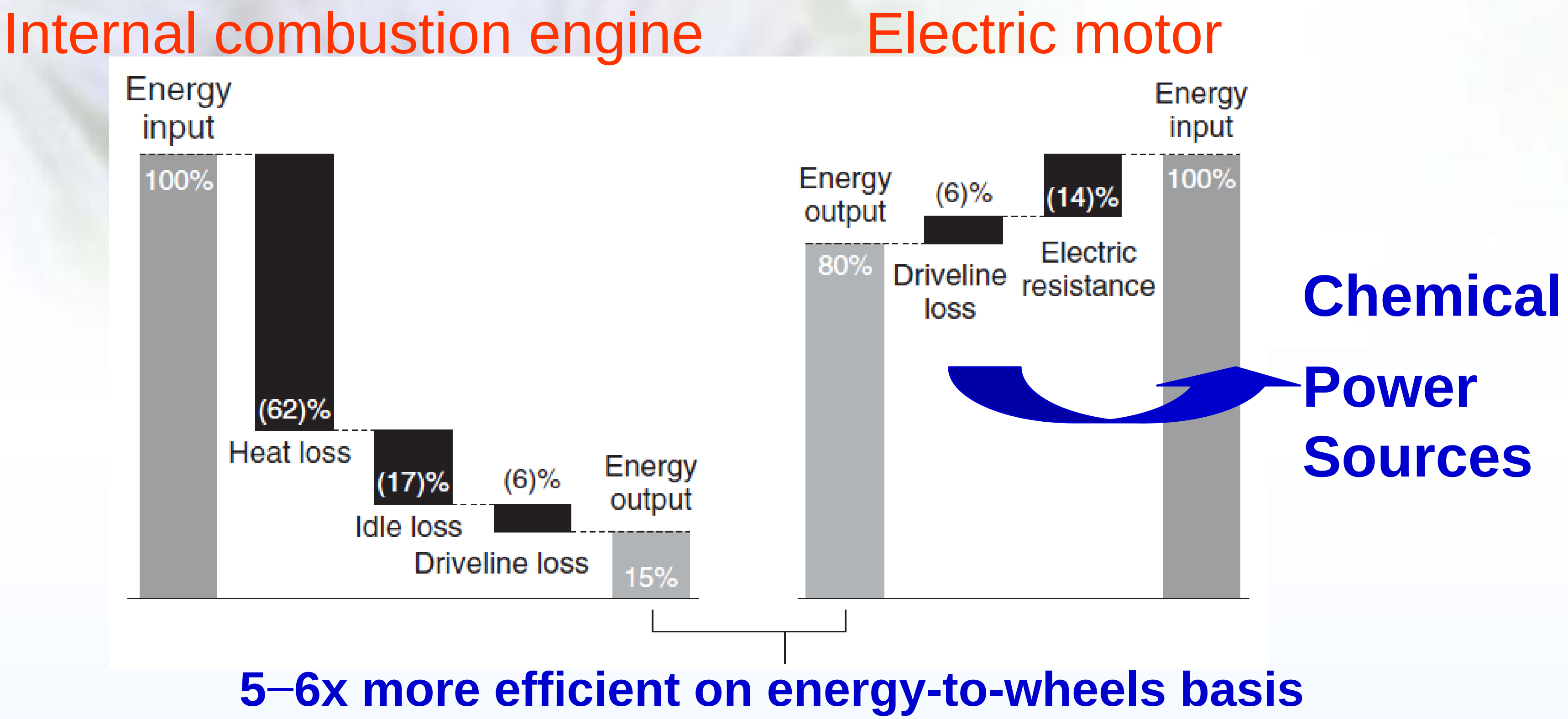
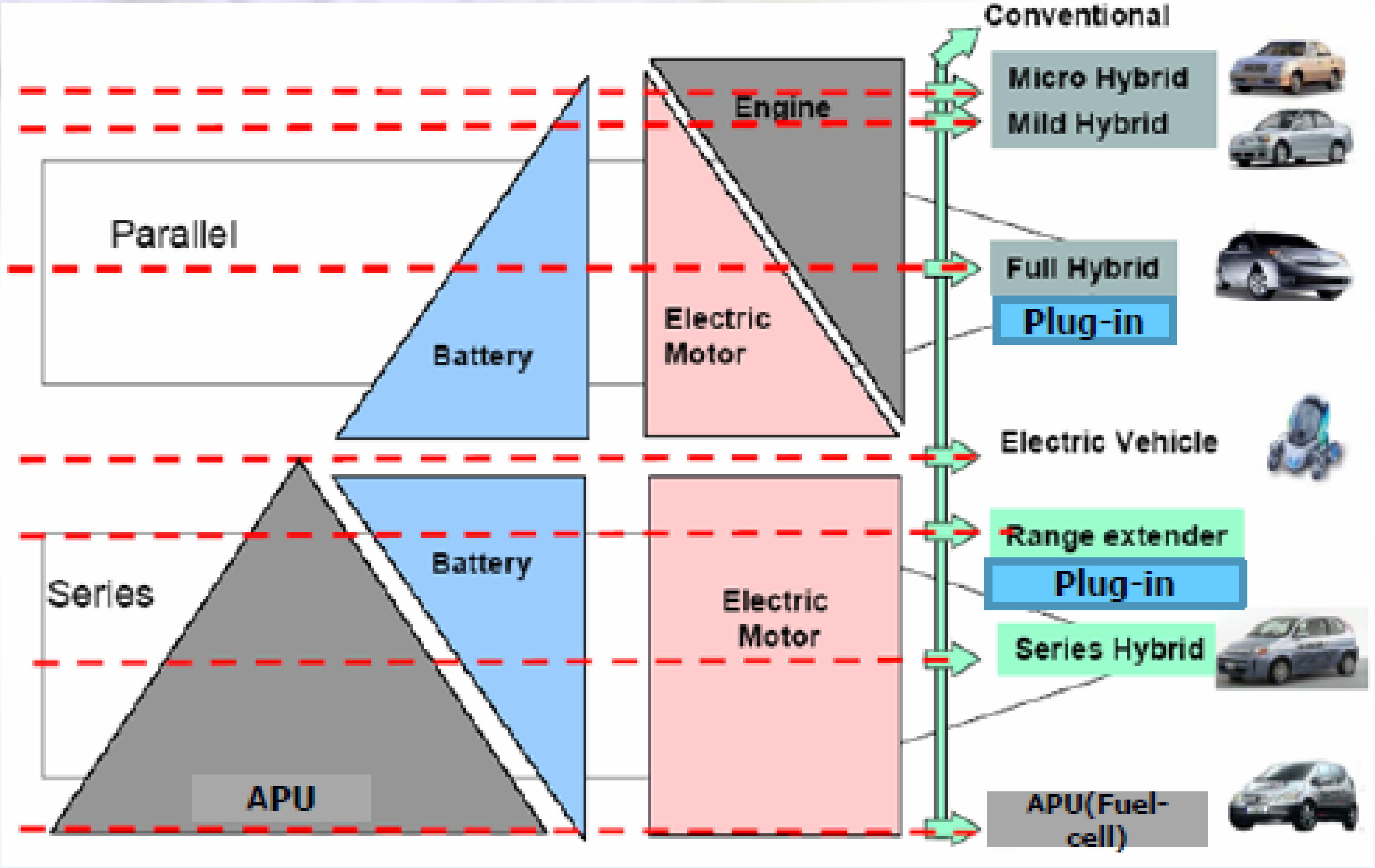


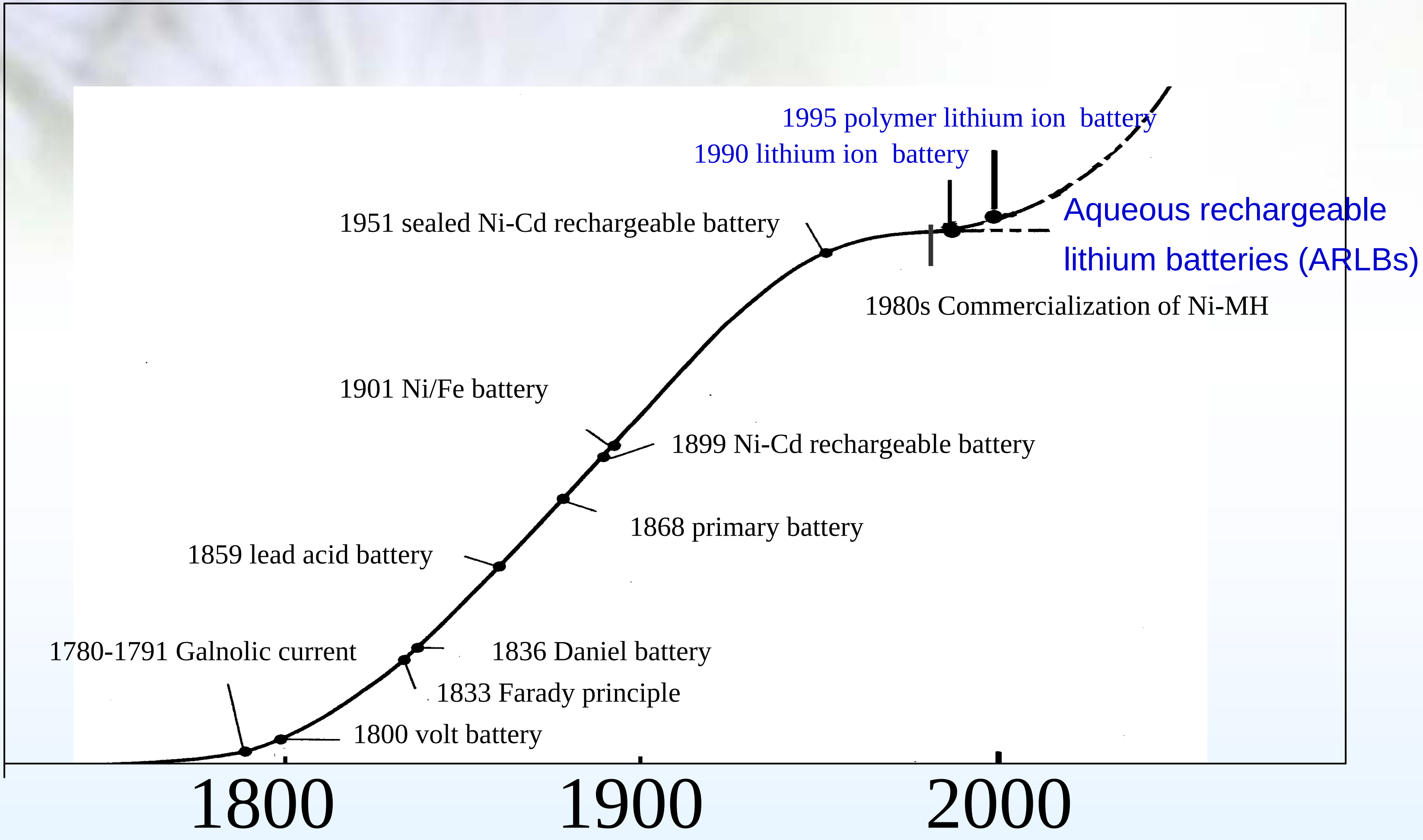
Fig. Comparison of an internal combustion engine with an electric motor on energy-to-wheels basis.

- Reduce environmental impact: reduce 20% CO_2 emission and 40-90% urban air pollutants
- Improve grid optimization: idle capacity of the power grid can supply 70% energy needs of today's cars and light trucks.

Species of Electric Vehicles



History of the development of chemical power sources



Wu et al., Lithium ion batteries-Practice and Applications, Chemical Industry Press, 2004.

Chemical Power Sources

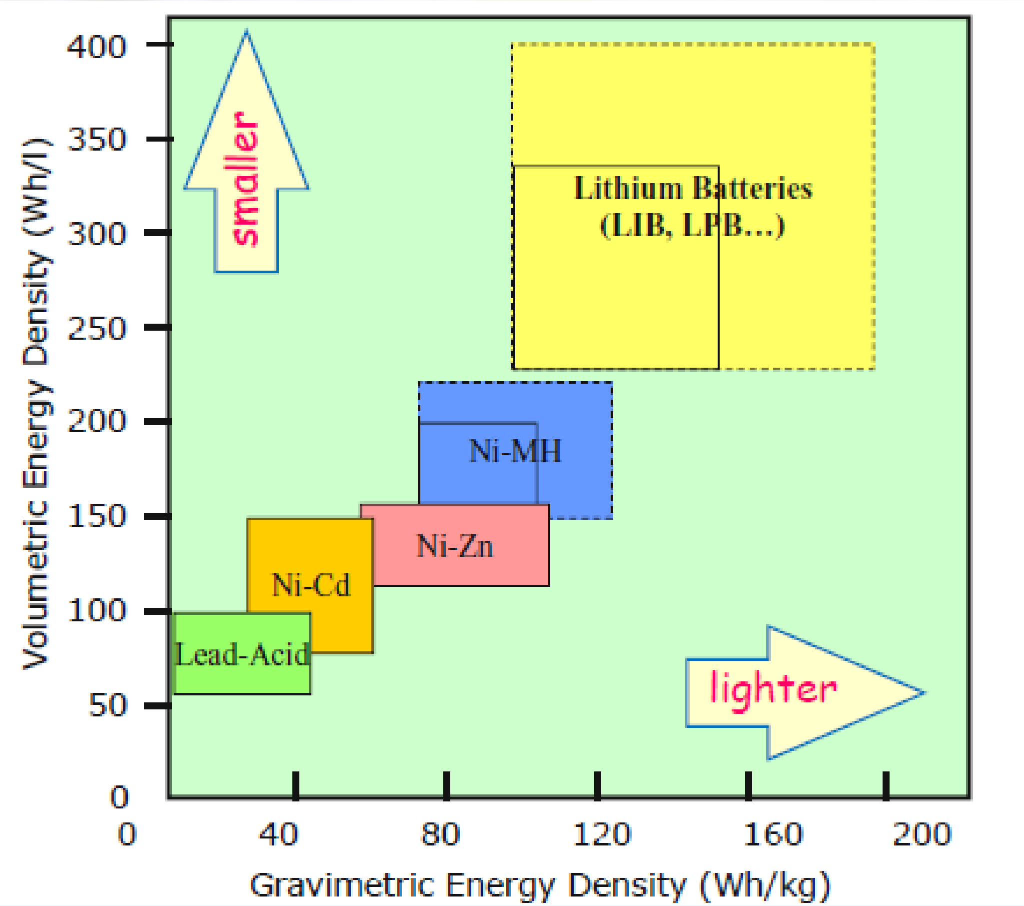
- Supercapacitors
- Polysulfide bromide battery (PSB)
- Zn/Br battery
- Vanadium redox couples (VRC)
- Sodium sulfur battery (Na/S)
- Lead acid battery
- Metal-air battery
- Ni-MH
- **Lithium ion battery**
- **Li/Air**
- **Aqueous rechargeable lithium battery (ARLB: 水锂电)**
- ……

2nd Symposium on Energy Storage and Power Batteries, Chengdu, 11-14 Nov., 2007

- Safety
- Rate capability
- Energy density
- Energy efficiency
- Cycling life
- Maintenance
- Capital cost for kWh
- Per-cycle cost

Power Sources for HEVs and EVs

- Smaller: higher volumetric energy density
- Lighter: higher gravimetric energy density

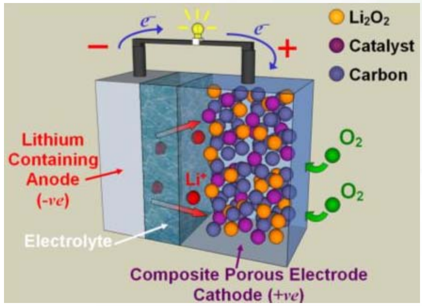


- Power density: charge and discharge performance

Lithium ion batteries at the present status are of practical value.

Li/Air Rechargeable Batteries

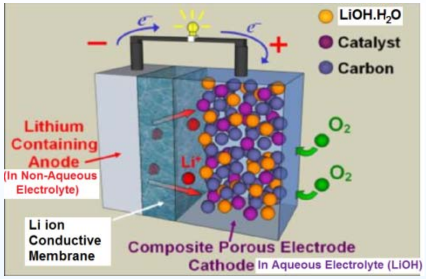
Theoretical Energy Density



1. Organic electrolytes in both anode and cathode electrodes
   - Overall reaction: $2Li+O_2=Li_2O_2$
   - Specific capacity: 3318 mAh/g (carbon), 1024 mAh/g (cell)
   - Cell voltage: 2.959 V
   - Energy density: 3031 Wh/kg

Air electrode porosity: 75%

2. Organic (in anode) and non-organic (in cathode) dual electrolytes
   - Overall reaction: $4Li+6H_2O+O_2 \rightarrow 4LiOH.H_2O$
   - Specific capacity: 1280 mAh/g (carbon), 488 mAh/g (cell)
   - Cell voltage: 2.982 V
   - Energy density: 1436 Wh/kg



References	Li metal	H_2
Specific capacity:	3862 mAh/g	13382 mAh/g
Energy density:	11600 Wh/kg at V_0=3V	15600 Wh/kg at V_0=1.169 V or 8700 Wh/kg at V_0=0.65V
Fuel storage efficiency:	~100%	~7-8%

J.P. Zheng, et al., *J. Electrochem. Soc.* **155**, A432-A437 (2008).

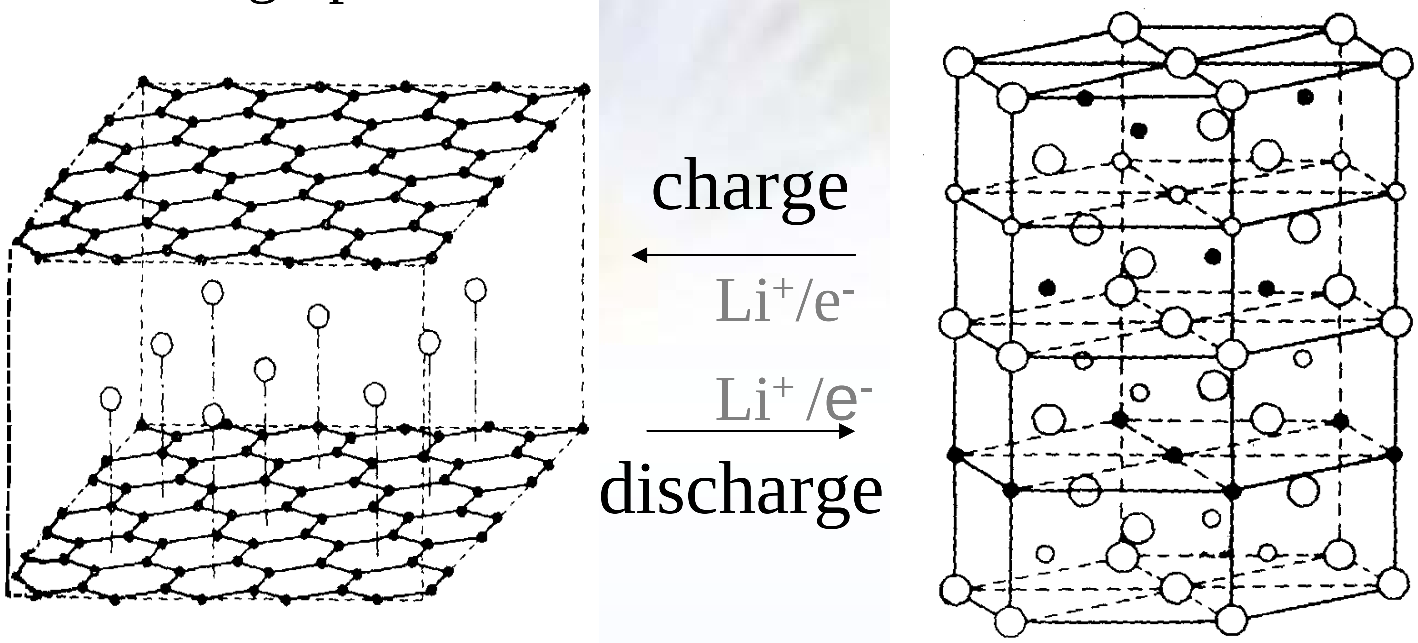
锂-空气电池面临的机遇与挑战

- Anode
  - Stable to moisture
- Cathode
  - High and good porosity
  - High oxygen diffusivity
  - High Li^+ conductivity
  - High electrical conductivity
- Membrane
  - High Li^+ conductivity
  - Low interface resistance to electrolytes
  - Mechanically strong and flexible
  - No liquid permeation (for due electrolytes cells)
  - Good chemical and electrochemical stabilities
- Electrolyte
  - High oxygen solubility
  - High Li^+ conductivity
  - High oxygen diffusivity
  - Hydrophobic (to organic electrolyte cells)
- Catalyst
  - High catalytic activity
  - Inhomogeneous catalytic activity

2. Principle of lithium ion battery

Anode: graphitic carbon

Cathode: $LiCoO_2$



$$\text{Anode: } 6\,C + x\,Li^+ + x\,e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_xC_6$$

$$\text{Cathode: } LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + x\,Li^+ + x\,e^-$$

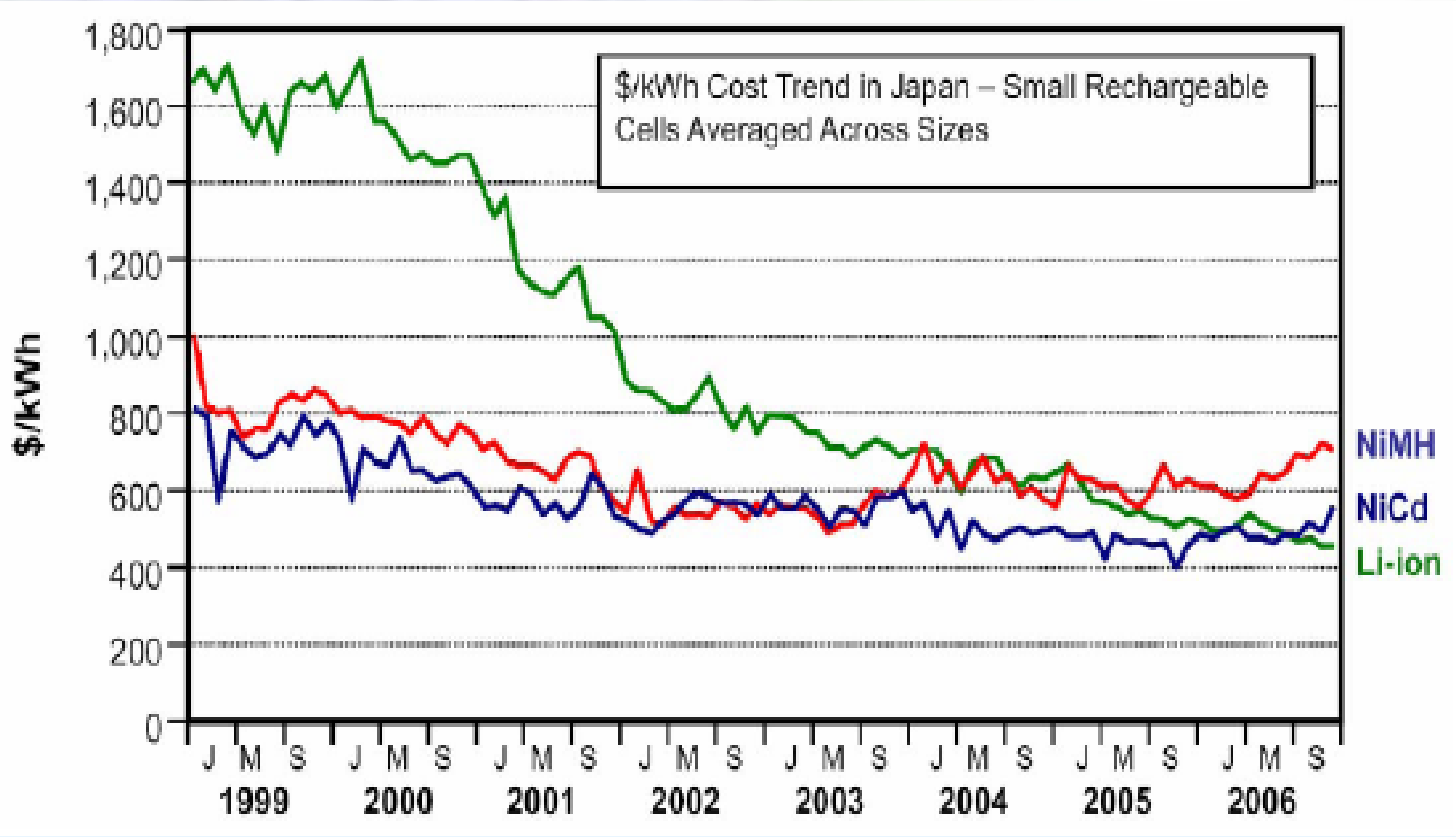
$$\text{Total: } 6\,C + LiCoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + Li_xC_6$$

Y.P. Wu et al., Lithium ion batteries: Practice & applications, Chemical Industry Press, 2004.

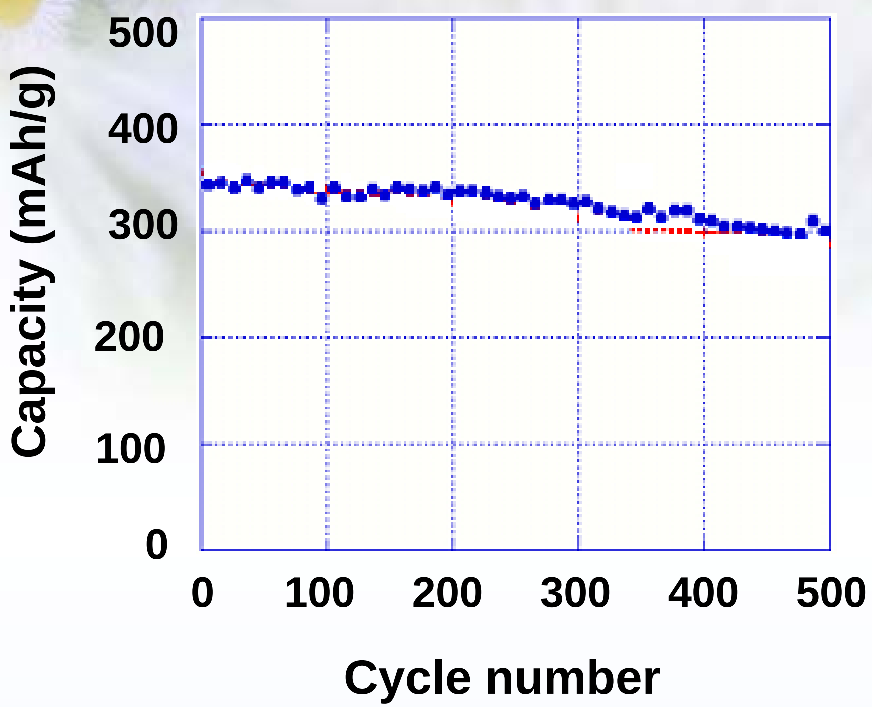
Characteristics of lithium ion battery:

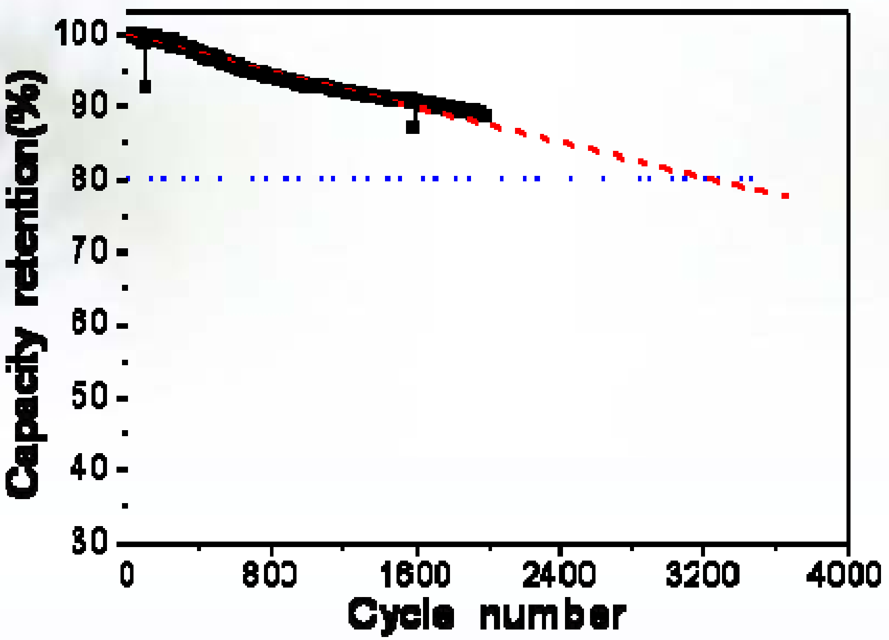
- High output voltage (average 3.6V) and power
- High energy density (UR18650: >450 Wh/cm^3, >200Wh/kg)
- Low self discharge (<10%/month)
- No memory effect
- Long cycle life (>1000 times)
- High rate capability (1C)
- High coulomb efficiency (near 100% except in the 1st cycle)
- Easy to measure the residual capacity
- Maintenance free
- No environmental pollution (green battery)
- Wide work temperature (-25 - +45^{o}C, extended to –40 – 70^{o}C)

Costs for Chemical Power Sources



√Price: anode and cathode





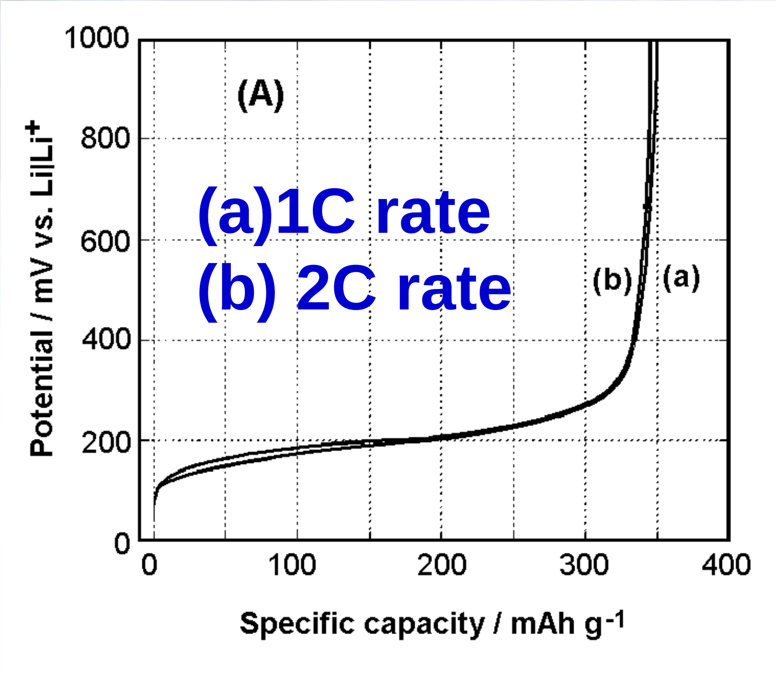
Anode: SSG based on natural graphite

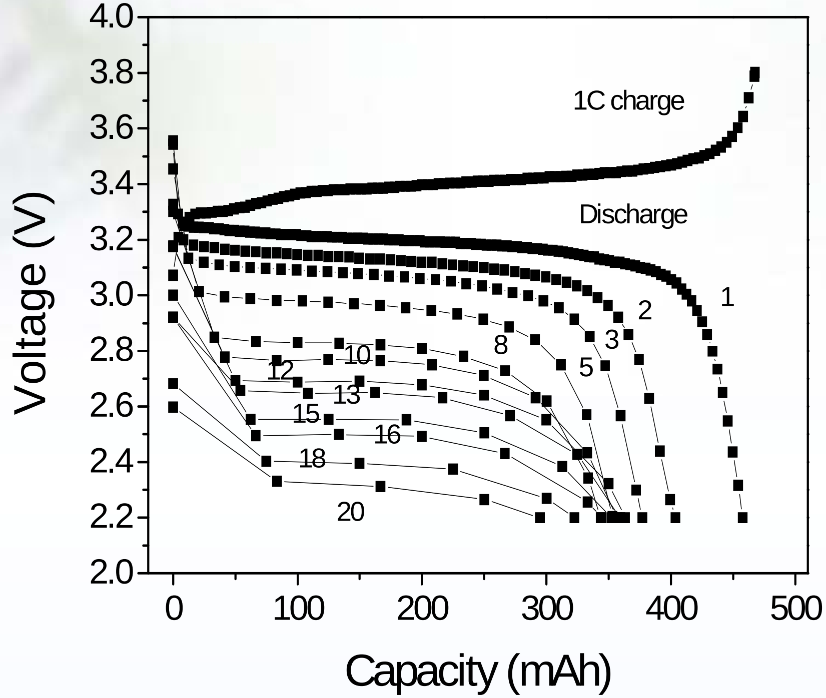
Cathode: $LiFePO_4$ and $LiMn_2O_4$

Excellent cycling: Low cost.

Y.P. Wu et al., J. Power Sources, 162: 663 (2006); J. Appl. Electrochem., 36, 1307 (2006).

√Rate capability: anode and cathode





1st cycle: 348 mAh/g
500th cycle: 301 mAh/g
86%

2C (348 mAh/g),
0.08C(357 mAh/g)
= 97.5%

SSG: Good success in market, very good product over the world.

Safety & Reliability ???

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. **Safety ???**

Nuclear Reactors

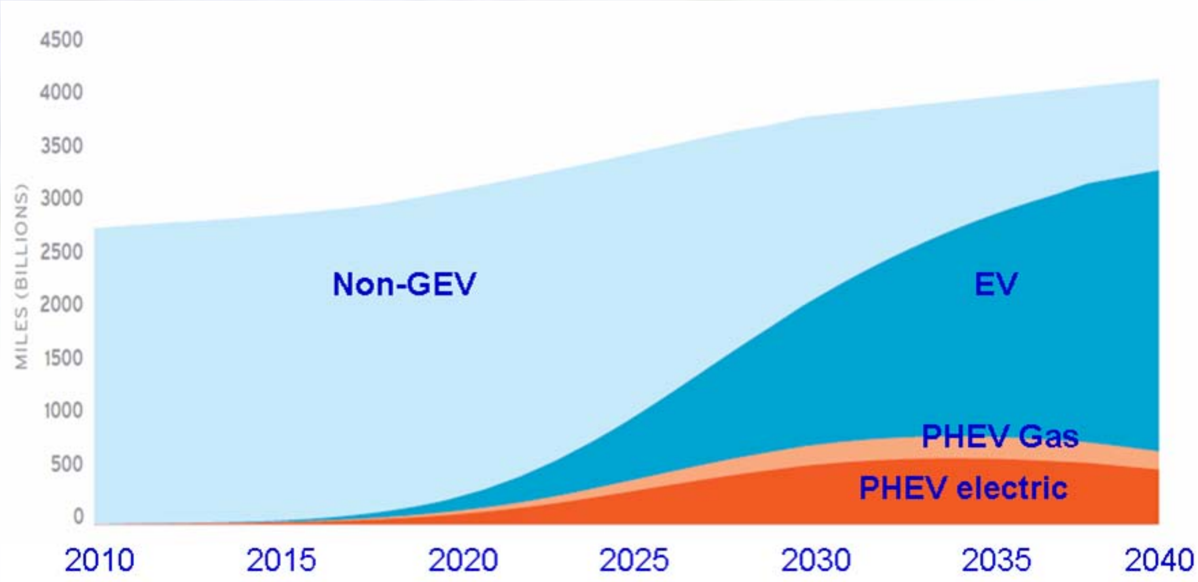
(a) 2008 (b) **2011.3.16**

Views of Fukushima Nuclear Reactors

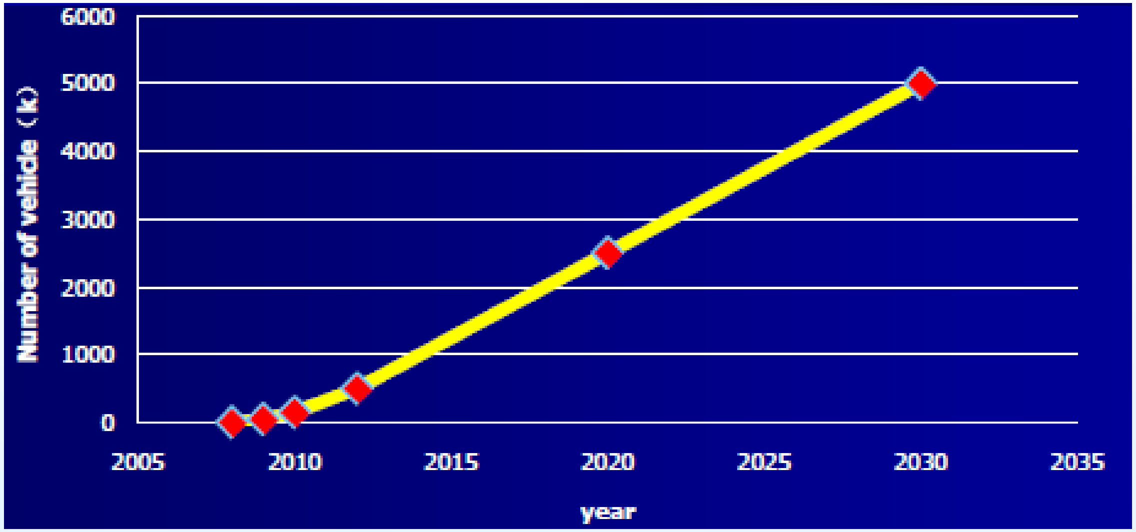
- If water sources or foods in the northeast of Japan is polluted by 137Cs, it is estimated that the east part of Japan will be turned into waste and could not be cropped.
- Emission elements from Fukushima reactors include ^{131}I and ^{137}Cs. Their decay half lives are 8 days and 30 yrs, respectively. The radiation danger in the long run can be at least 80 days and 300 yrs, respectively.
- ^{239} Pu was found outside of the reactors, indicating the destroy of the inner shells/vessels of the reactors. It half life is about 24110 yrs.

Expected Market for Future: USA and China

USA

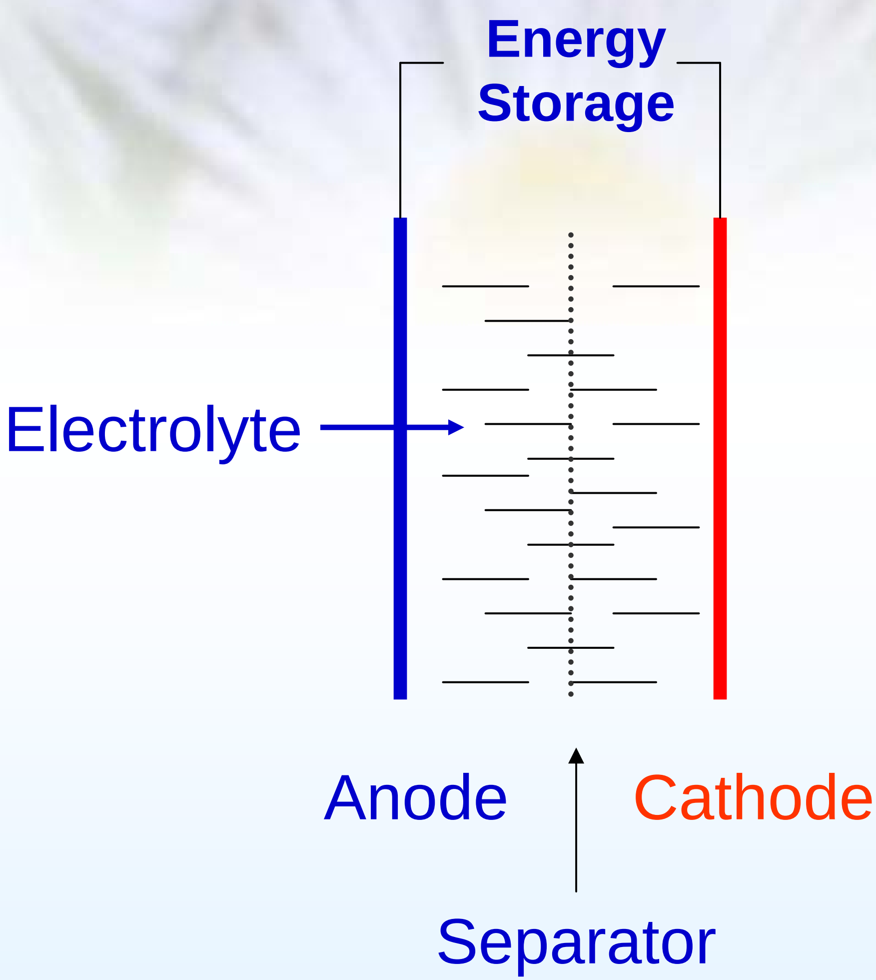


China



HEVs

Main Materials for Lithium Ion Batteries



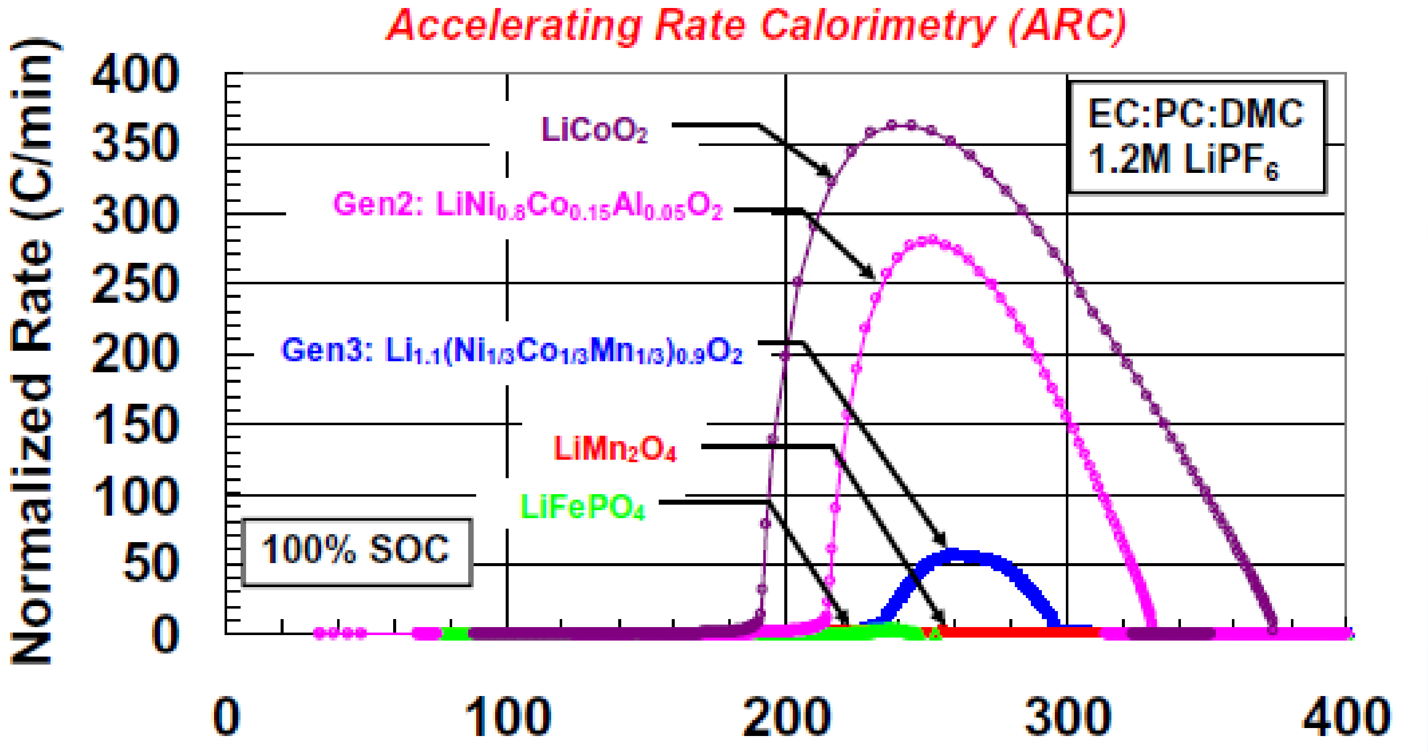
Inner safety

- Anode material
- Cathode material
- Electrolyte
- Separator

3.1 Cathode materials

Cathode	Safety	Energy density	Power density	Cycling life	Low temperature
NCA	Fair	High	Middle	Fair	Fair
NMC	Good	High	Middle	Long	Fair
LMO	Very good	Middle	High	Poor	Good
LFP	Very good	Low	High	Very long	Poor

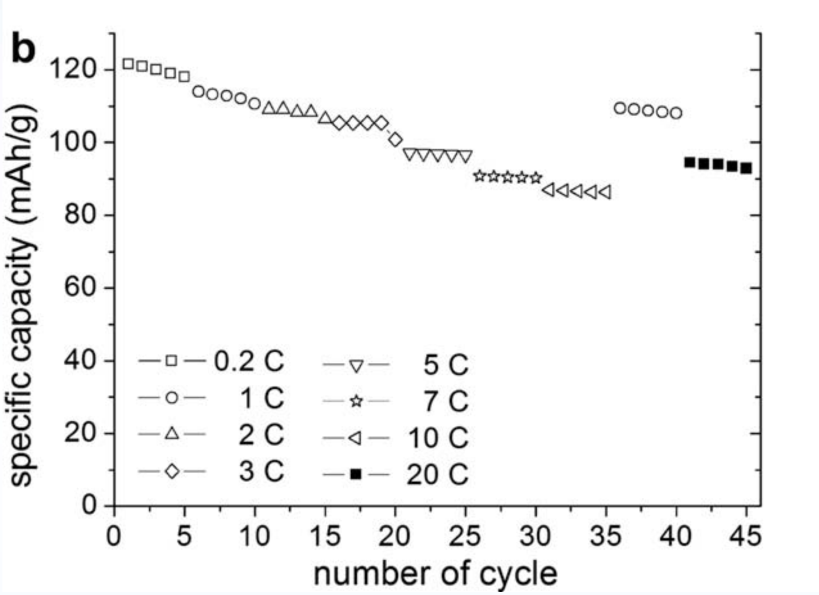
Thermal Behavior for Some Cathode Materials

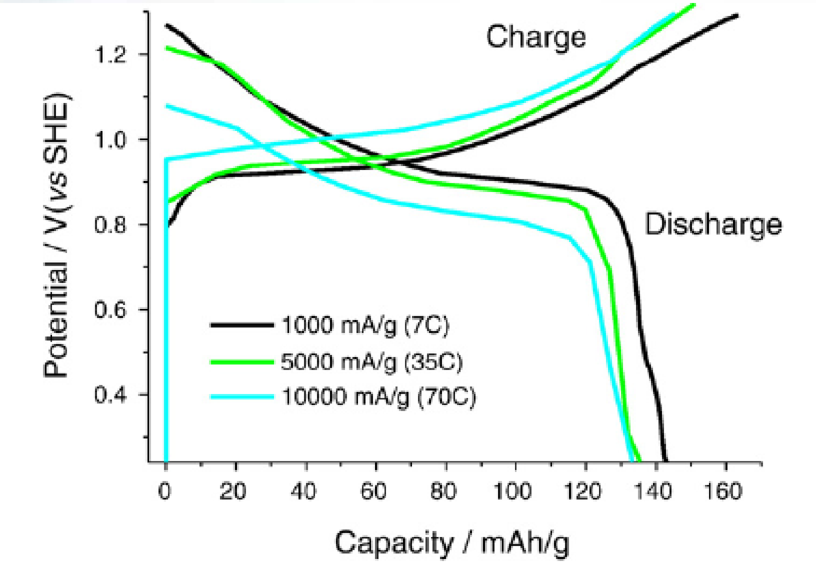


Temperature (°C)

Our pioneering research on nanostructured $LiCoO_2$ cathode materials

Our nano $LiCoO_2$



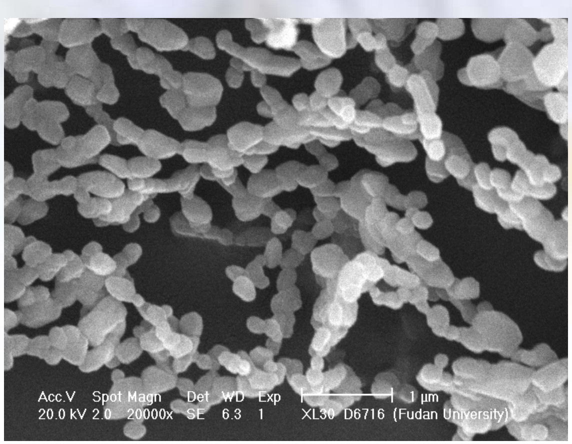


$LiCoO_2$ from traditional solid-state reaction in aqueous electrolytes: Results from Stanford University.

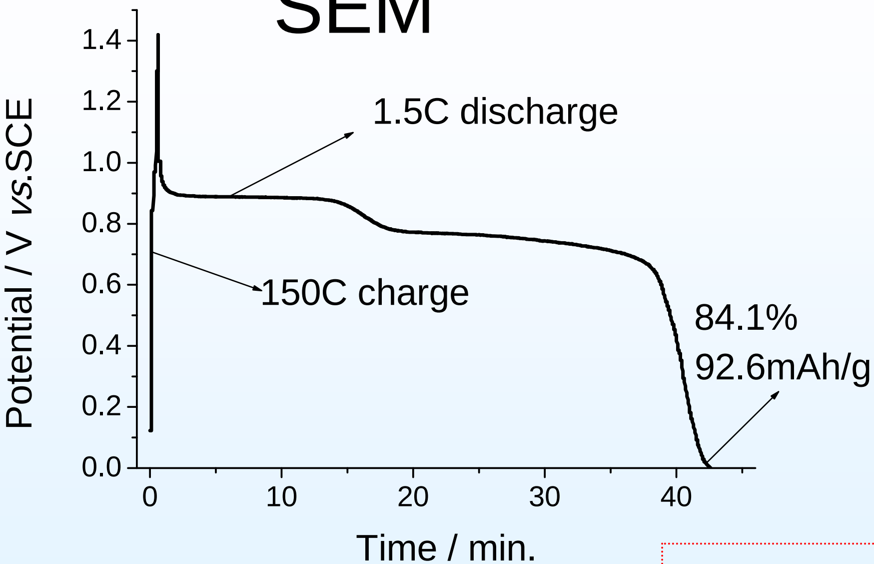
Our nano $LiMn_2O_4$: very good charge-discharge behavior for high power density.

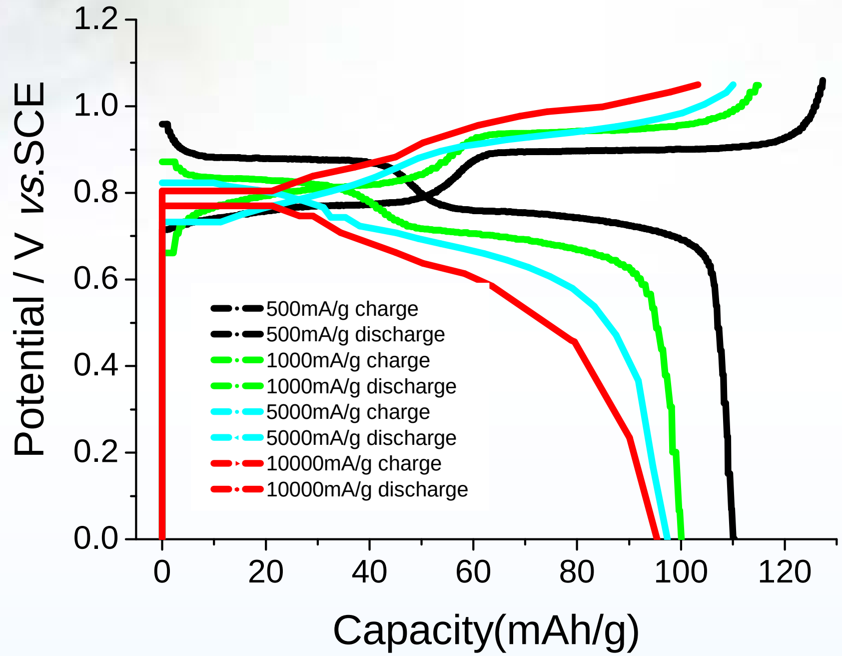
Wu et al., *Electrochem. Commun*. 11 (2010) 1524.

Nanochain $LiMn_2O_4$: Ultra-fast charge capability



SEM





Charge/discharge curves at different current densities

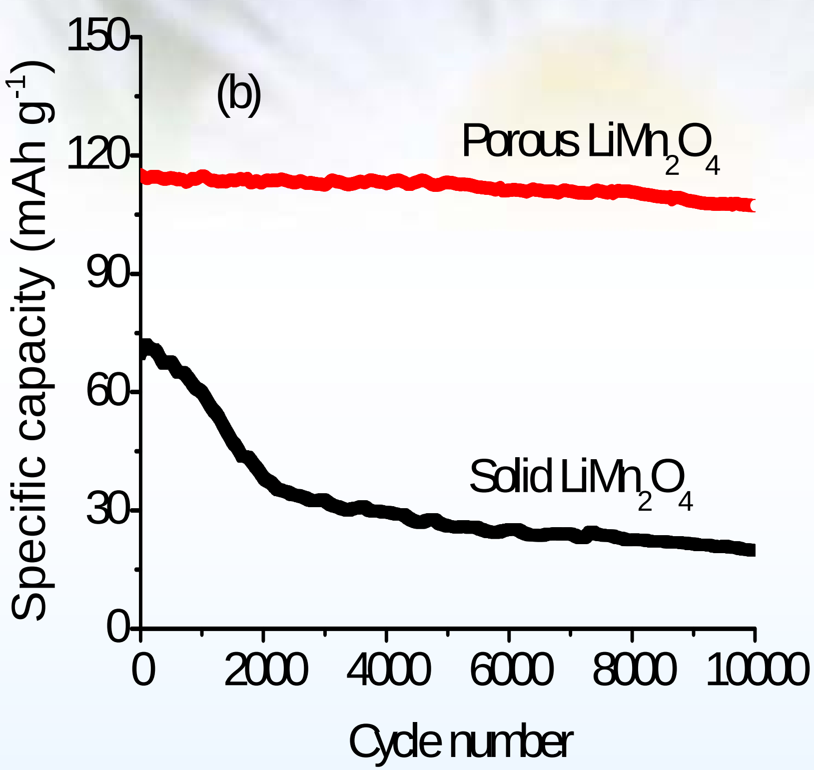
Ultra-fast charge performance

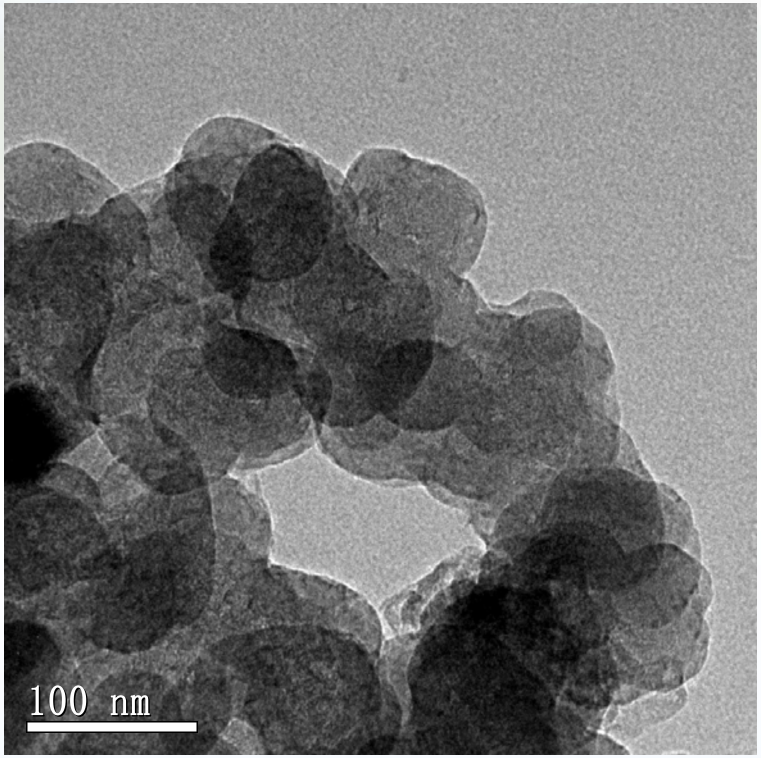
Wu et al., *Electrochem. Commun.*, 13 (2011) 205.

Good crystal, nano grain and porous structure

No acid: pH ~7

Excellent cycling behavior





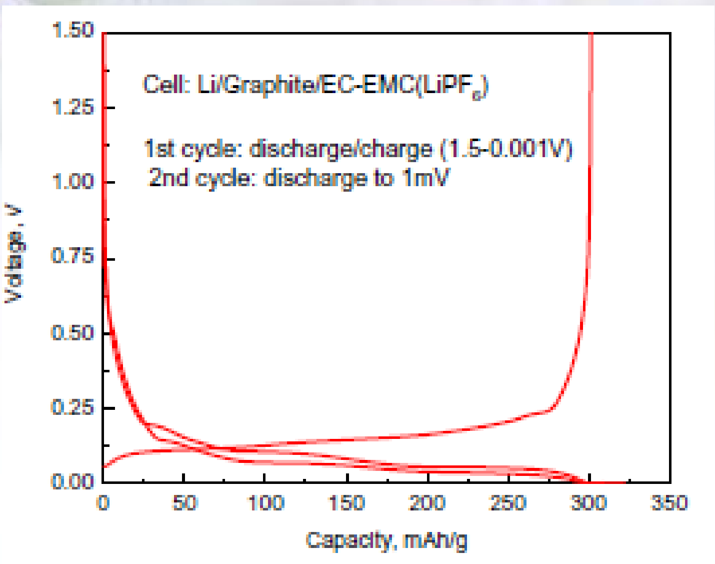
TEM of porous $LiMn_2O_4$ after 10000 cycles.

Stable morphology and crystal structure after 10000 cycles.

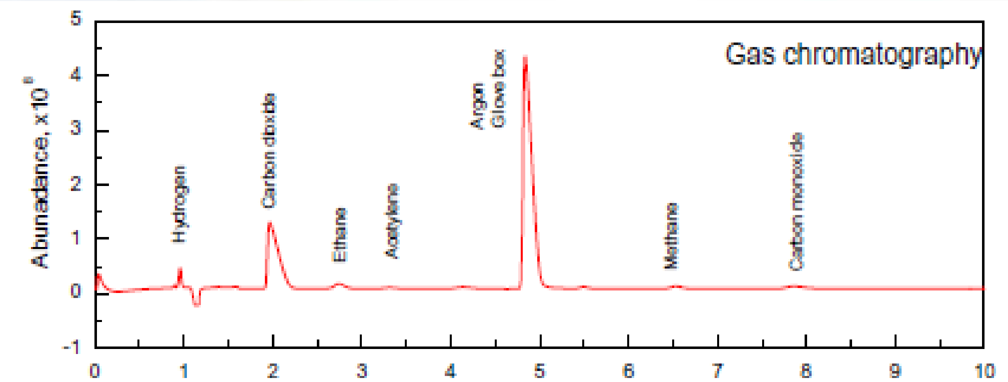
3.2 Anode materials

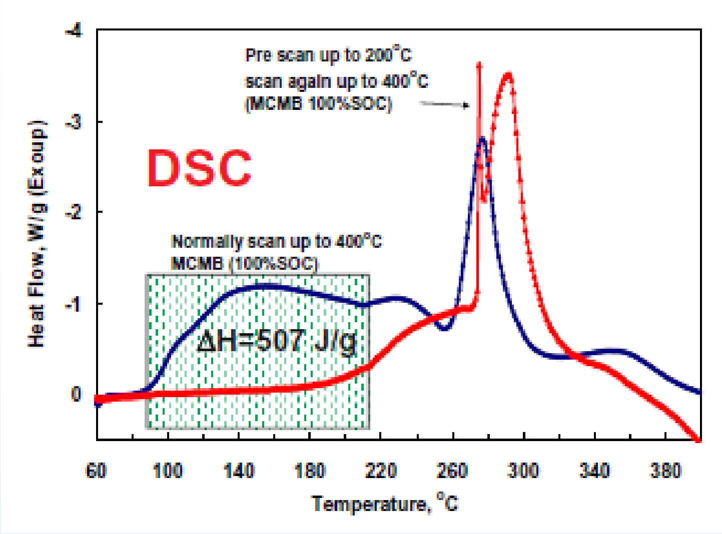
- Graphitic carbons
- Sn-Co-C
- Composite of graphitic carbon and Si
- $Li_4Ti_5O_{12}$
- ……

√ Safety



After exposing charged carbon/Li cell at 100ºC for several hours.





The thermal heat generated by the continuous breakdown and formation of the SEI (80~200ºC) could trigger the early thermal run away.

MCMB: ΔH : 1552 J/g

Preheated MCMB: ΔH : 1045J/g

Heat from secondary SEI: ΔH=507 J/g

Si-based anode materials

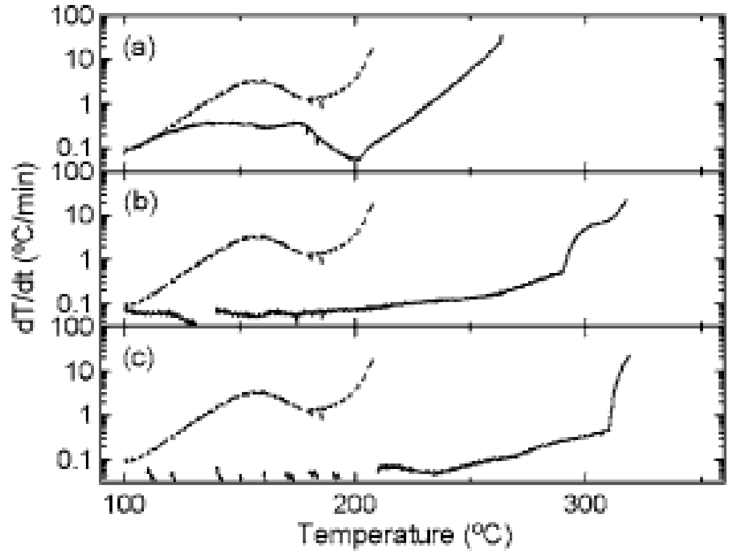


Fig. Self-heating rate *vs* temperature for 100 mg $Li_{0.81}C_6$ (dashed line), 40 mg Li_1Si, 20 mg Li_2Si, and 15 mg Li_3Si solid line in 40 mg EC/DEC.

⬇

Si is safer than carbon anode materials.

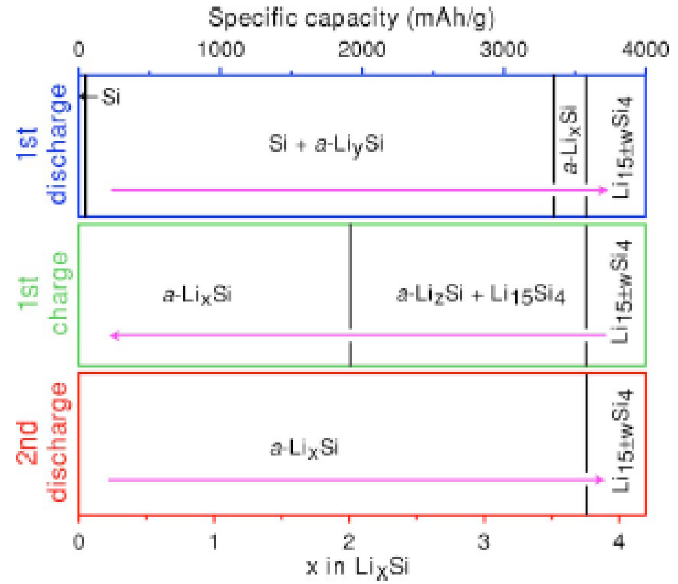


Fig. Phase diagram describing the phases that form during the charge–discharge cycling of a Li/Si electrochemical cell between 0.005 and 0.9 V at room temperature.

⬇

Large capacity.

Si and graphite composite anode as materials

- Si + SSG

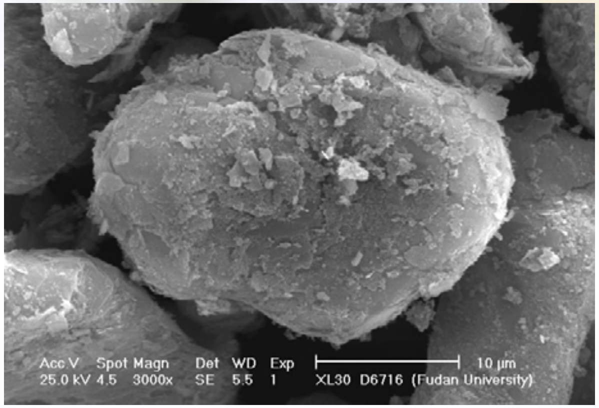


Fig. SEM micrograph of 10% nano Si-coated SSG.

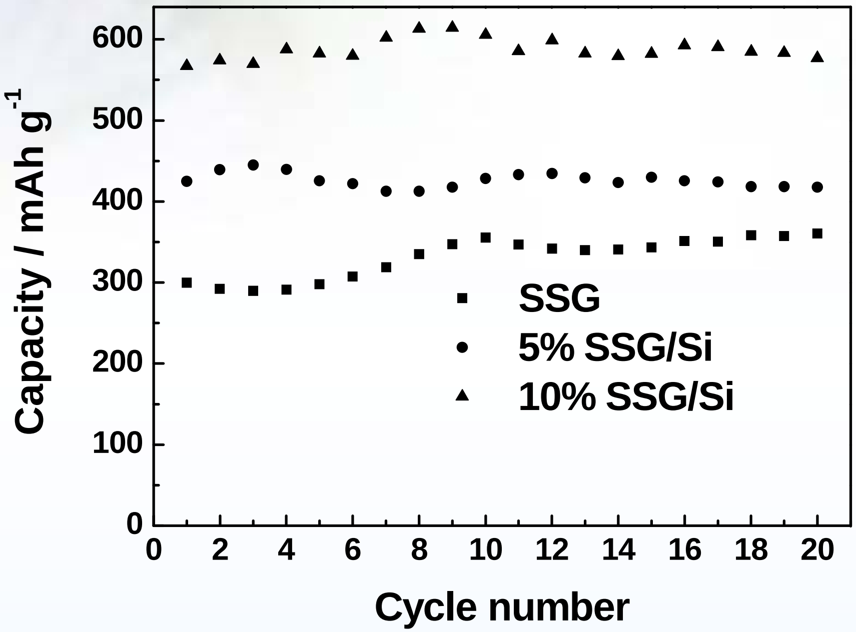
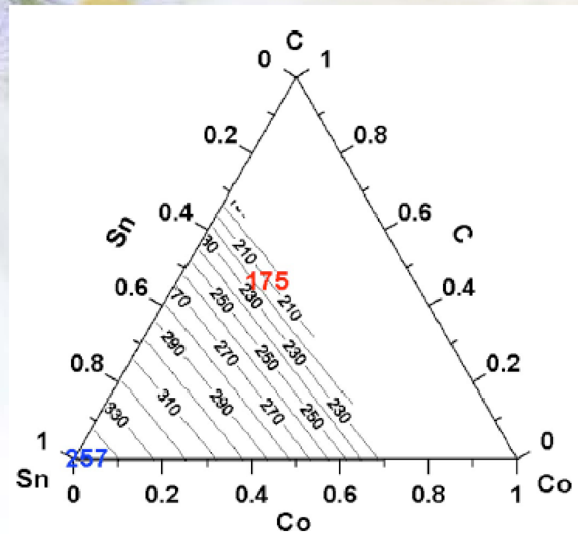


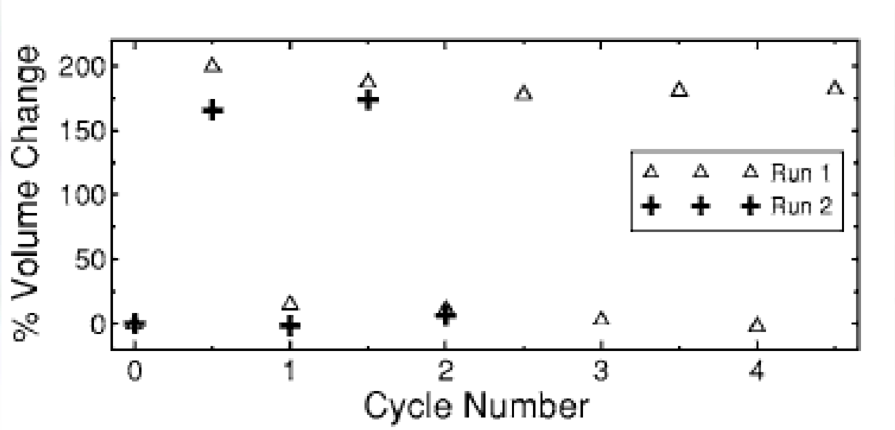
Fig. Cycling behavior of SSG, 5% and 10% nano Si-coated SSG cycled between 0.01 and 2.0 V with a constant current density of 0.2 mA/cm^2 (0.2 C for the pristine SSG) for 20 cycles.

Wu, et al., *J. Mater. Chem.* 17, 1321 (2007)

Sn-Co-C

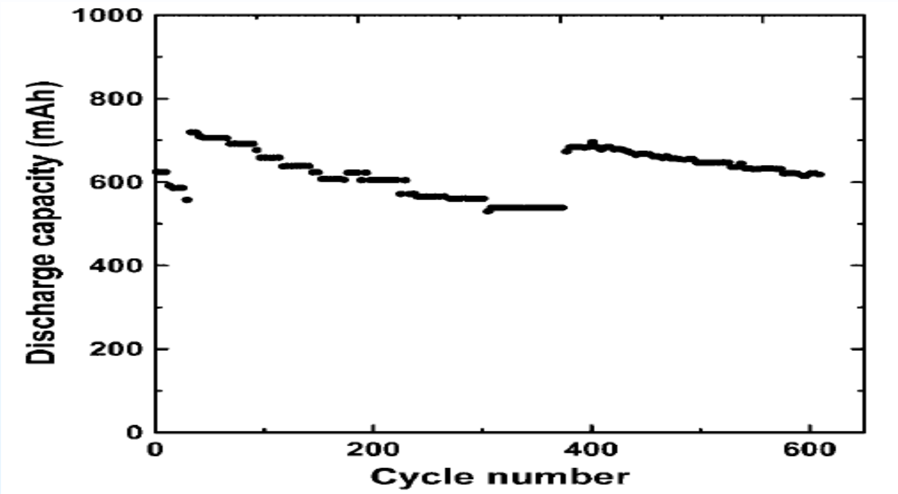


Volume expansion for a-$Sn_{0.34}Co_{0.19}C_{0.47}$.



Volume expansion *vs* cycle number for an a-$Sn_{0.34}Co_{0.19}C_{0.47}$ patch reacting with Li.

Though about 175% volume change, good stability.

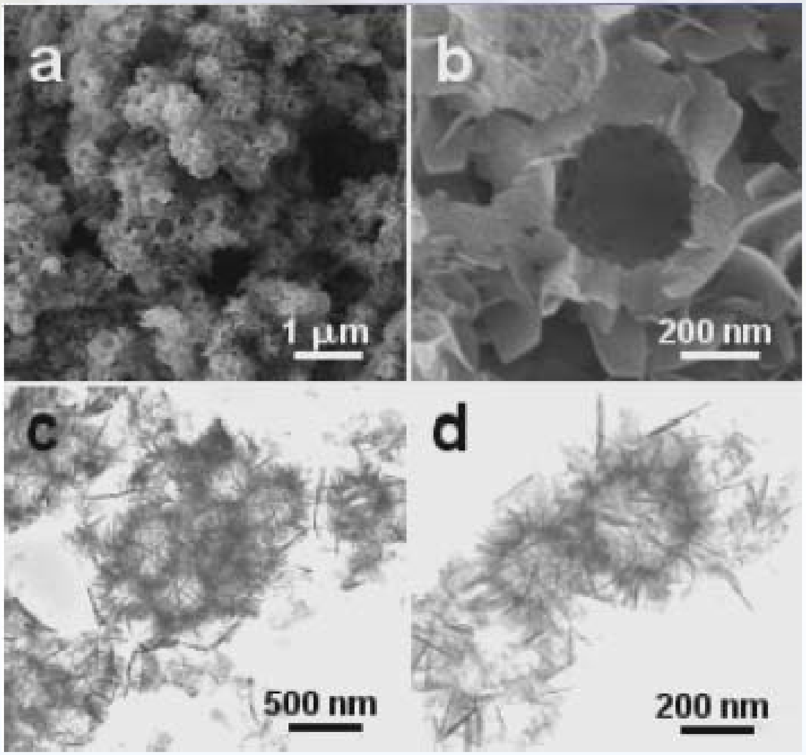


Sony:

Mainly for videos

This cell was cycled at 1C rate for the first 30 cycles, charged at C/3 and then discharged at 1C for cycles 30–375 and charge–discharged at a C/3 for the remaining cycles.

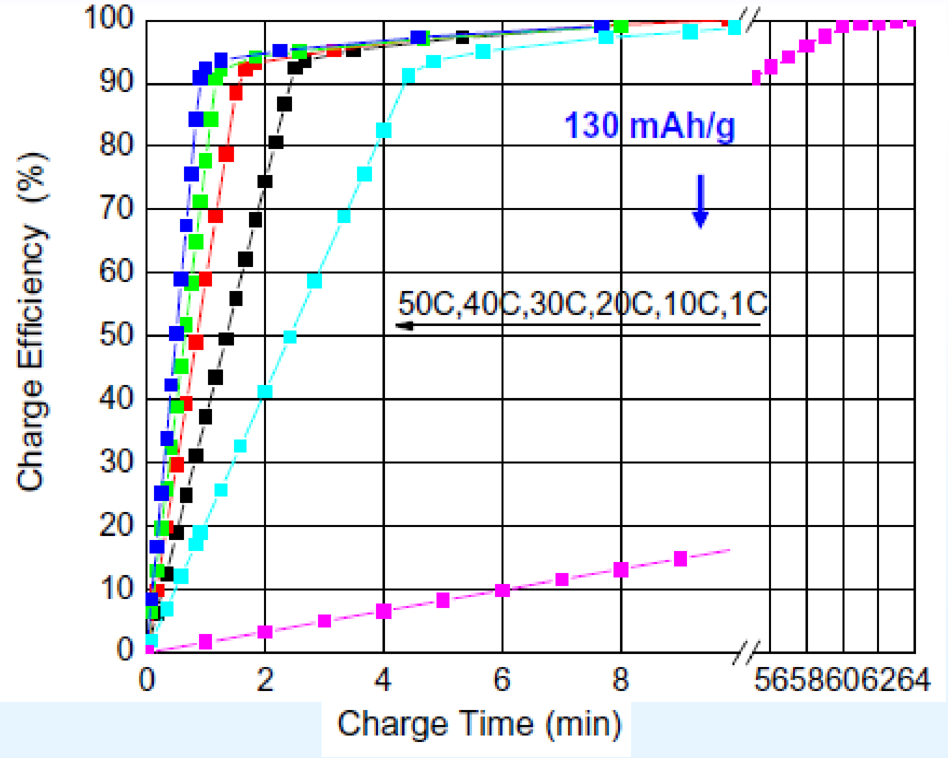
LTO: $Li_4Ti_5O_{12}$



Hollow microsphere

Low energy density

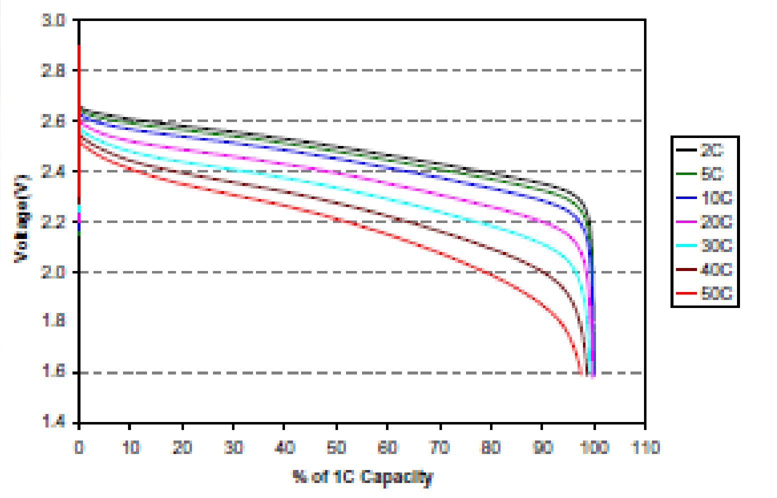
Rate capability

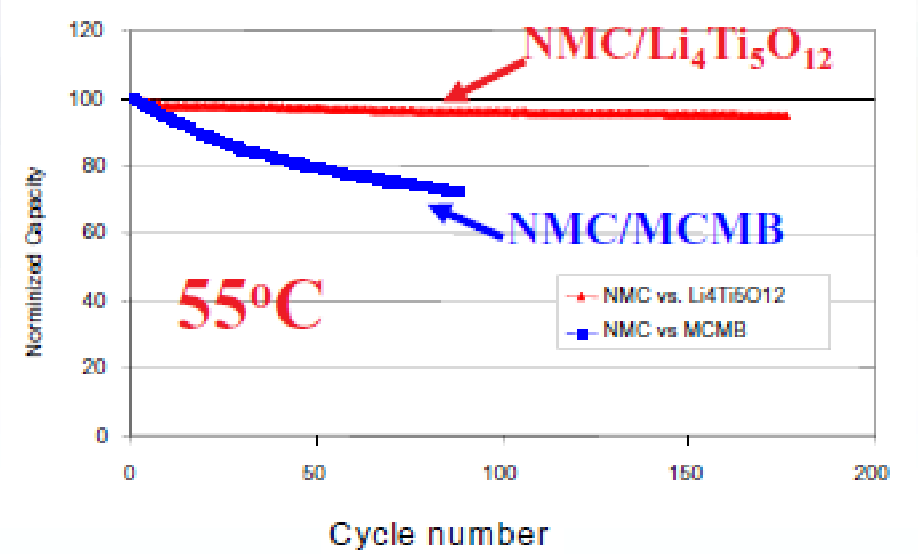


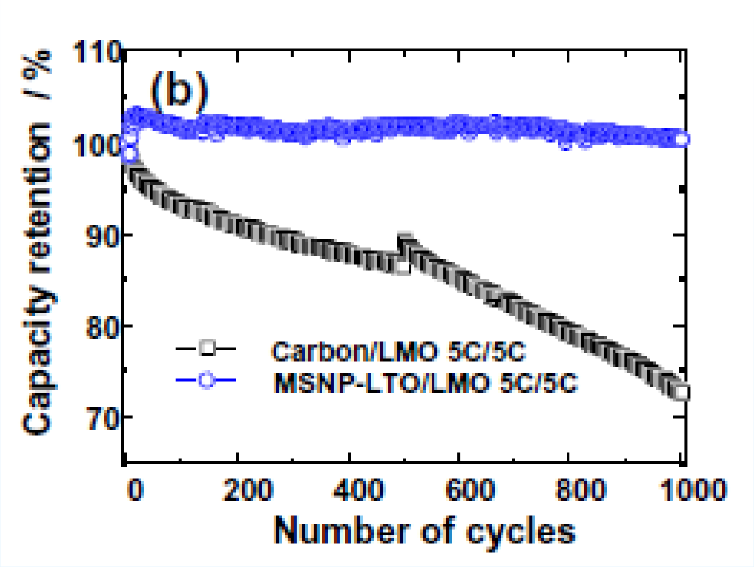
Electrochim. Acta 2009, 54, 6244

Batteries based on LTO

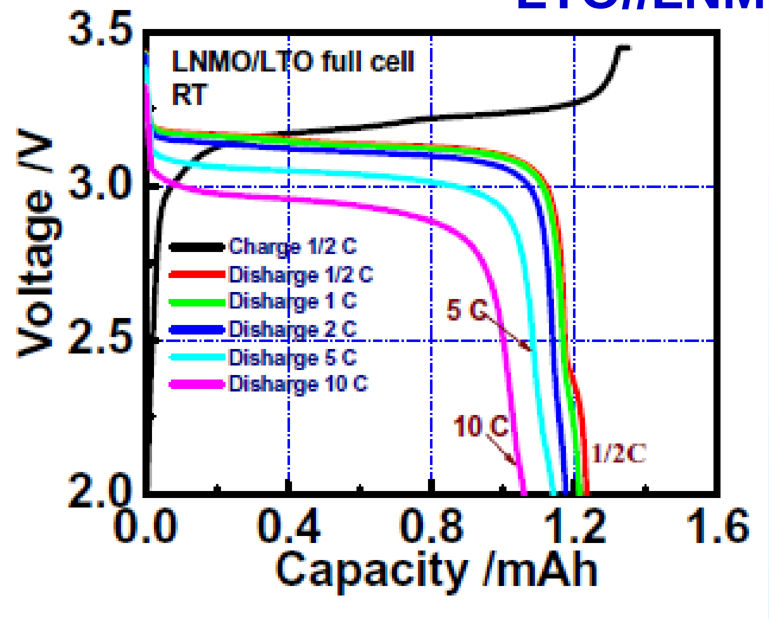
LTO//LMO







LTO//LNMO



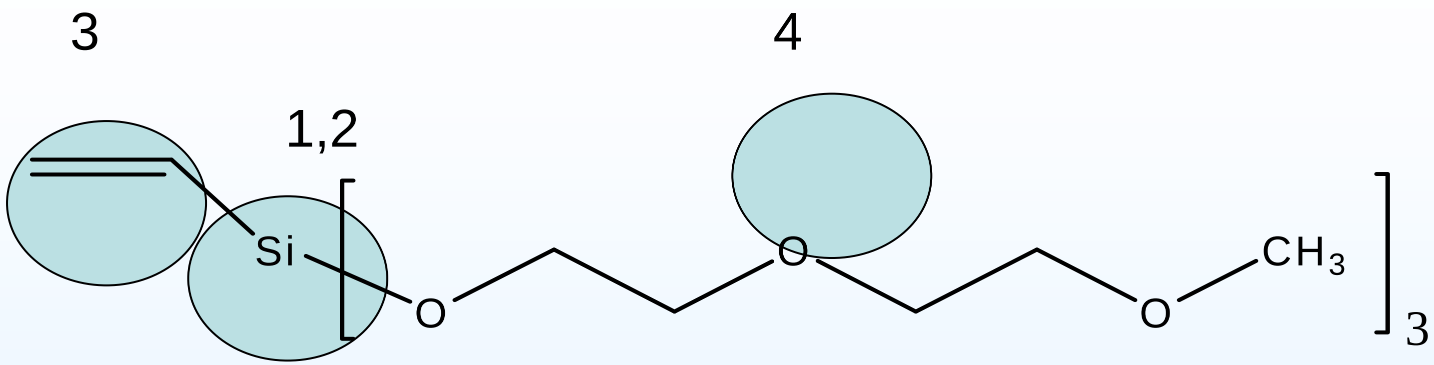
3.3 Electrolytes

- Liquid electrolytes
- Solid electrolytes
- Gel electrolytes

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

Safety during Abuse

Field Failure

– Manufacturing defects

• Loose connection, separator damage, foreign debris

• Can develop into an internal short circuit

• Can lead to overheating and thermal runaway

Abuse Failure

– Mechanical

• crush, nail penetration

– Electrical

• short circuit, overcharge

– Thermal

• thermal ramp, simulated fire

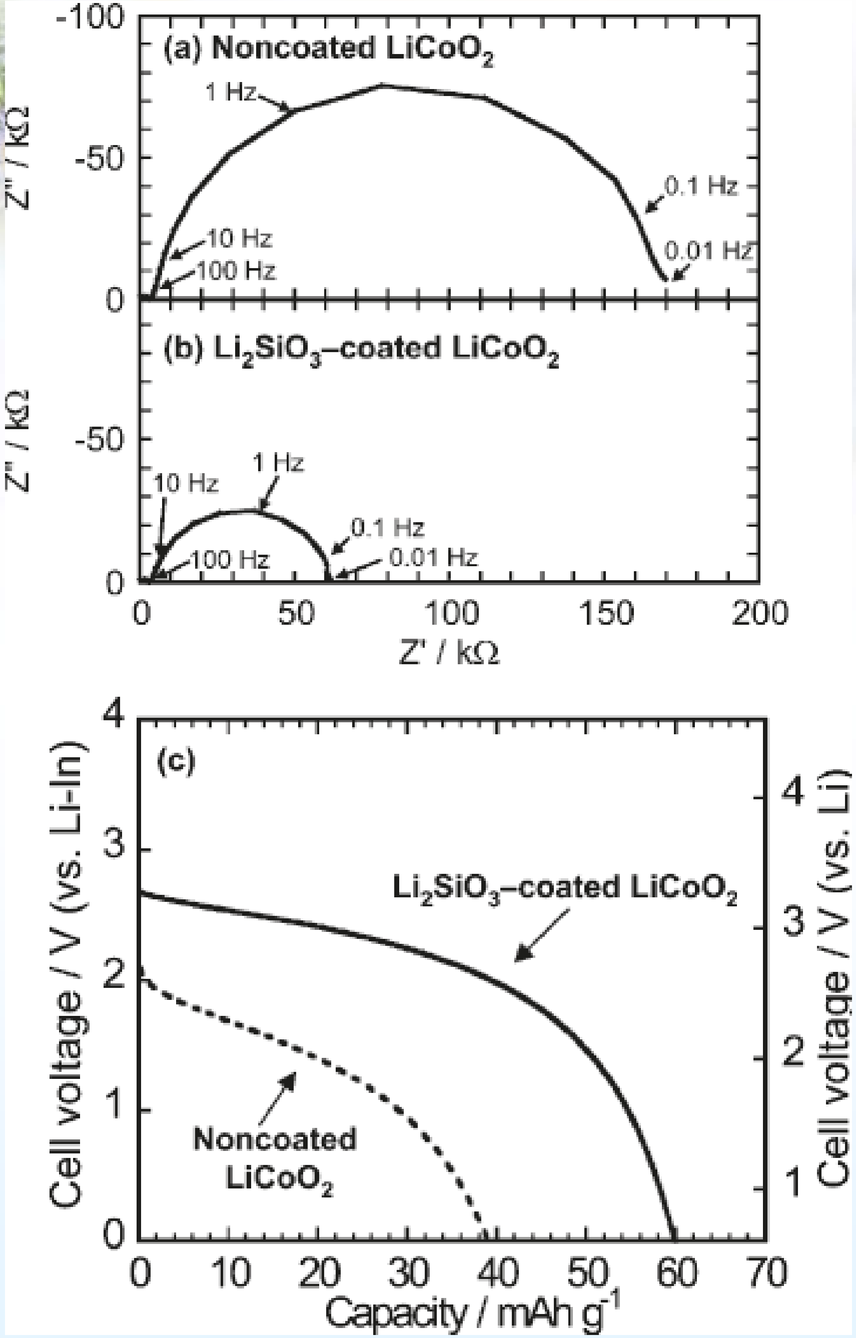
A123: PHEV (Jun. 2008)

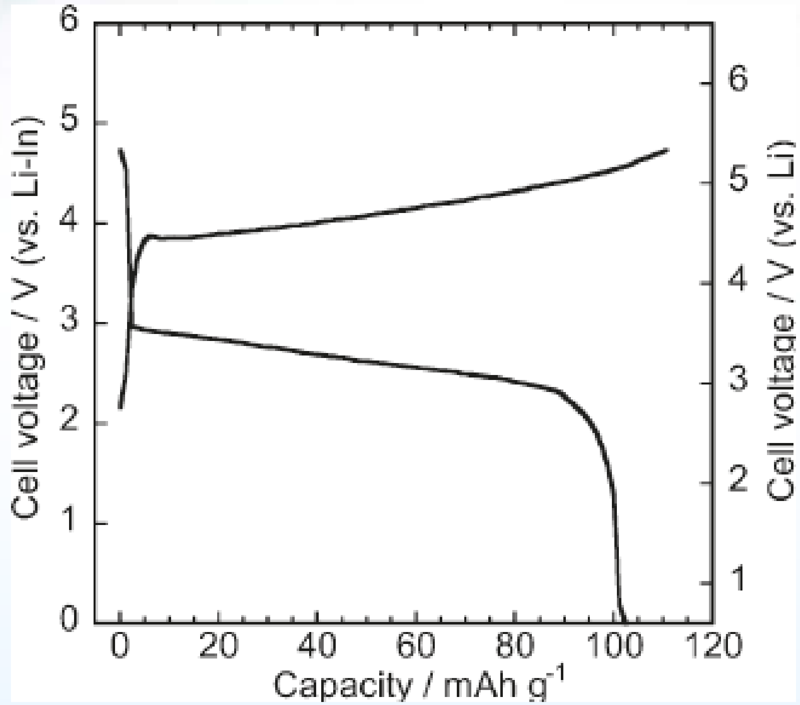
(April. 2011)

A flammable, solvent-based electrolyte is used.

Solid electrolyte

- Interphase improvement
- Processing ability



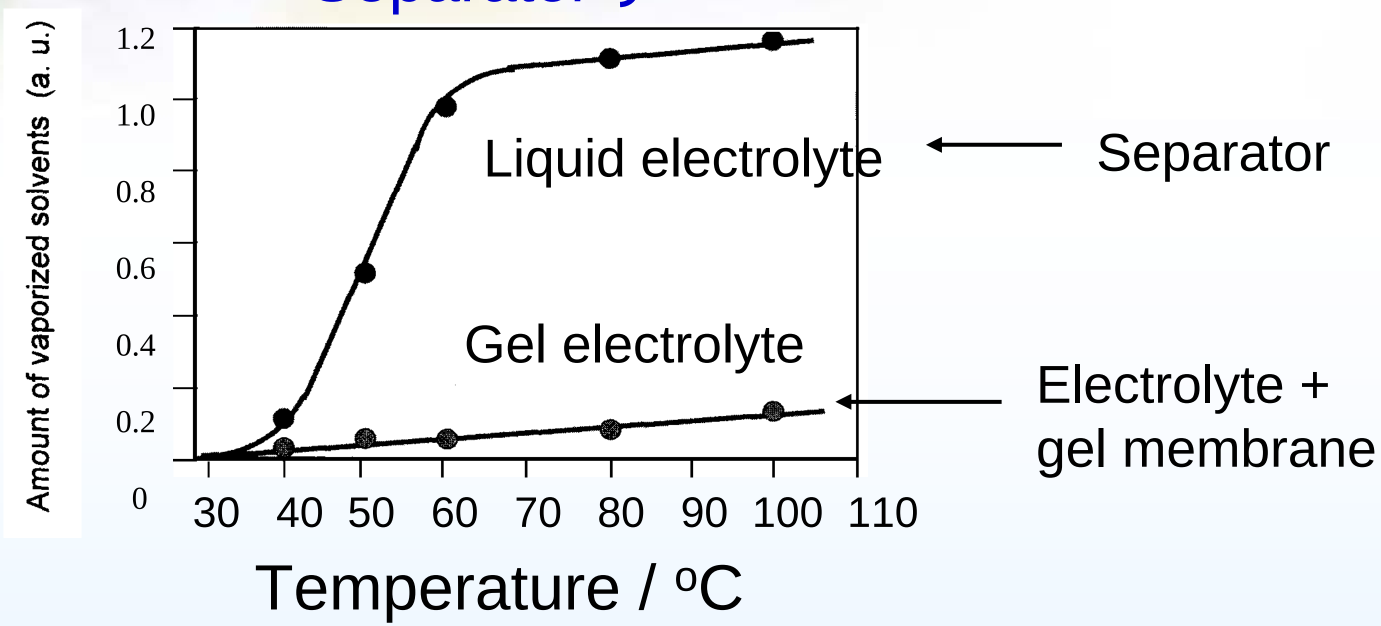


$Li/Li_2S\text{-}P_2S_5$ solid electrolyte/Li_2SiO_3-coated $LiCoO_2$

What will be the next step ?

Safety → Anode, Cathode, Electrolyte, Separator

Electrolyte, Separator → Gel electrolytes

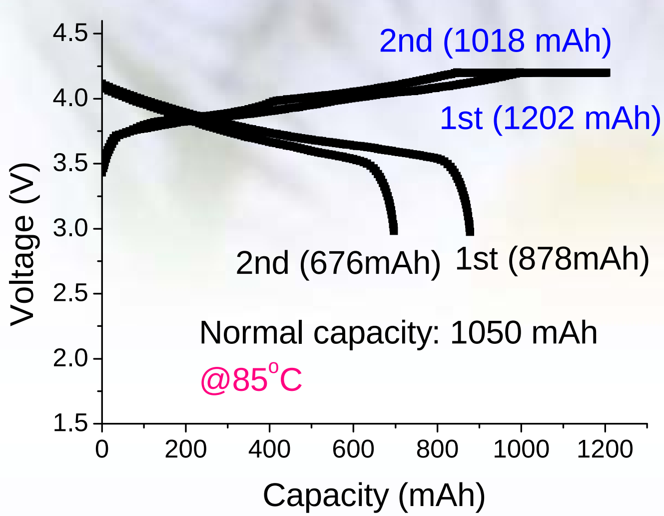


Gel membranes:

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

Some GMs (Gel membranes)

Graphite/GM/$LiCoO_2$



GMs: Self-distinguishing

2 cycles: total time 6 hr and 9 mins
Thickness: from 6.3 mm to 7.5 mm
Storage: full charge @85ºC 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.

Traditional separator:
Heat shrinkage and combustibility

Wu et al., unpublished

Advantages & disadvantages of GMs

	Separators	GMs of Japan & South Korea	GMs of Fudan
Main components	PE, PP	PE, PP, PMMA	PVDF
Demands on equipments	Very high	Very high	Fair
Manuf. process	Fair	Complicated	Simple
Non-combustibility	**Poor**	**Poor**	**Very good**
High temp.	**60^oC**	**85^oC**	**85^oC**
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**

4. Summary

- **Safety & reliability, cost and environmental problems for lithium ion batteries are the challenging problems for energy storage.**

- **More demonstration especially for long term is necessary to get the first-hand data for electric vehicles.**

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- Sanyo Chemical

Group members’ hard work

Study Tours to Shanghai Expo (2010)
(China Pavilion)

Study Tour to Xi’an (2011)
(The top of Hua Mountain to watch sunrise)

Thanks for your kind attention !