Key challenges and new trends in battery research

Jean Marie TARASCON
Flash recall on why energy storage …
EU and French research structuring initiatives …

Rapid assessment of today’s state of the art in Li-ion battery

✓ Spot/highlight present limitations and upcoming issues (recycling)

✓ Present ongoing research activities to tackle them

✓ Mention/discuss a few chemistries beyond Li-ion

Conclusions ?

✓ Personal view of the future of batteries
✓ A few comments beyond science
PHYTOLOGICAL SYNTHESIS

-CHOH-

CO₂ + H₂O → C₆H₁₂O₆ + 6 O₂

7 kWh/kg

Millions of years

BIOMASS

FOSSIL FUELS

13 kWh/kg

95 MBa /day

SUN

ENERGY

HYDROGEN

-CHOH-

O₂

H₂O

CO₂

Energy

COMBUSTION

Discovery

Consumption

Projected discoveries

28 TW

8.2 Billions tep/hab

14 TW

6 Billions tep/hab

World Annual Consumption

10¹⁰ tep

17.7

10

5

892760012

13:00 aujourd'hui

3.7 Billions tep/hab

6 Billions tep/hab

3.7 Billions tep/hab

Consommation Mondiale Annuelle (10¹⁹ tep)

8.2 Billions tep/hab

6 Billions tep/hab

Billions de barils /an

Années

Découvertes à venir

Consommation

Réserves découvertes

gap

Renewable Energies

WHY ENERGY STORAGE?
Energy storage: Another challenge of the 21st century

To improve-create new energy storage technologies

To better handle the renewable energy resources of our planet
- Wind
- Solar
- Oceans

MWh kWh

To favour the development of electric vehicles
- Electric
  kWh

To develop better electrochemical energy storage devices

Chemical

Batteries

Electric
Restructuring of the scientific and technological landscape via the creation of new federative tools
European Initiative: ALISTORE-ERI
Launched in 2004 (FP6) with the incorporation of industries in 2008

The Research/Innovation/Education Triangle

18 European Research Labs

ALISTORE-ERI Industrial Club composition

15 members

EDF
Saft
Arkema
Umicore
Solvionic
Honeywell
Solvay
ESA
TOTAL
BASF
Sasol
CEA
Renault
Volkswagen
Robert Bosch

Business of industrial club members

Car makers
Material Makers
Battery Makers
Cell-phone makers
Aeronautic & Space users
PV’s users

ELITE (75 k€/an)  SILVER (25 k€/an)
To ensure a continuum from research to development via prototyping and then a quick transfer to our industries.
Primary cells

Rechargeable (Batteries)

Jan Hajek

Li / S

Primary cells

Genealogic tree for Li-based batteries

From Broussely (adapted)
The Li-ion technology:
A versatile technology in terms of potential

Non-aqueous electrolyte

LiCoO$_2$-NMC
4.2 - 4.6 V

Li$_x$Ti$_5$O$_{12}$
1.5 V

LiMn$_2$O$_4$
4.2 - 5 V

Li$_2$FeSiO$_4$
3.0 V

LiFePO$_4$
3.45 V

LiFe$_x$C$_6$
0.2 V

Li$_x$Si$_y$
0.4 V

Li$_2$FeSO$_4$F
3.6 - 4 V

TiO$_2$(B)
1.8 V
The Li-ion technology: a versatile technology in terms of power

Supercapacitors

Battery
The Li-ion technology:
a large potential market

18650
5-10Wh

EV's pack
30-100kWh

Different energy domains

Different materials

Different safety and cost aspects

...... Wh → kWh → MWh ......
Today’s state of the art performance for the Li-ion technology

Is it sufficient for EVs applications?
Challenges Facing batteries for EVs applications

- Higher Safety
- Higher Energy
- Higher Rate
- Lower Cost
- Sustainability
- Foresight

Materials/processes having the minimum environmental footprint and lowest possible life cycle cost

500 € /kWh

Cost / 2

Energy

x 2

130Wh/kg

*Source: Nedo (2009)
The Li-ion batteries: Sustainable aspects
The way we are making batteries today:

Fabrication of a battery of 1 kWh

Energy needed ≈ 287 kWh  CO₂ rejected: ≈ 110 kg

Need to make more sustainable and “greener” Li-ion batteries

Life Cycle Analysis of Large-size Li-ion secondary batteries, K. Ishihara et al. (2009)
Tomorrow’s needs and challenges: Develop sustainable Li-ion batteries

Ideal Situation

Routes followed

• Elaboration of inorganic materials via **eco-efficient** processes
• Use of organic materials as **renewable** Li electrodes
• Other chemistries: **Na-ion**
Towards energy saving processes for materials preparation

Ceramic process
Solvothermal process
Hydrothermal process
Ionothermal process
Bio-mineralization process

Lower temperatures → Economy of atoms

Towards energy saving processes for materials preparation

Bulk
700°C
Solid state reactions

120°C

180°C
Solution reactions

200°C

60°C
Nano
Ionothermal approach to the synthesis of inorganic compounds

**Ionic liquids**
Molten salts at ambient temperature

- No vapour tension
- Thermal stability > 300°C
- Non flammable
- Good solvent for numerous salts and polymers
- Cations-anions combinations (estimated at 15000, 1000 realized)

Synthesis at ambient pressure up to T= 300-350°C
Solvent recycling: classic organic route
→ washing CH₂Cl₂-centrifugation

Ionothermal synthesis of LiFePO$_4$: The case example

\[
\text{LiH}_2\text{PO}_4 + \text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} \xrightarrow{\text{EMI-TFSI}} 220-250^\circ\text{C} \xrightarrow{} \text{LiFePO}_4 + 3\ \text{H}_2\text{O} + \text{CO}_2
\]

Ionic liquids as reacting media:
Beneficial Aspects

- Synthesis of numerous known phases at $T = 200^\circ C$ (ceramic routes $T \approx 700^\circ C$)
  - $\text{LiFePO}_4$
  - $\text{Na}_2\text{Fe(Mn)}\text{PO}_4\text{F}$
  - $\text{Li}_2\text{FeSiO}_4$
  - $\text{LiFe(Mn)}\text{PO}_4\text{F}$

- Changing and adjusting the size and morphology of the powders
New electrochemical active materials
Via ionothermal synthesis

New family of **Fluorosulfates** $\text{AMS}_2\text{O}_4\text{F}$, $\text{A} = \text{Li, Na}$; $\text{M} = \text{Fe, Ni, Co}$

$$\text{MSO}_4 \cdot \text{H}_2\text{O} + \text{LiF} \xrightarrow{\text{EMI-TFSI}} \text{LiMSO}_4\text{F}$$

**Tavorite**

$\text{P}-1$

**Sillimanite**

$\text{Pnma}$

**Triplite**

$\text{C}2/c$

$\text{LiFeSO}_4\text{F}$

$\text{LiZnSO}_4\text{F}$

$\text{LiMnSO}_4\text{F}$

$3.6 \, \text{V}$

$140 \, \text{mAh/g}$

Unstable: Decompose for $T > 320 ^\circ \text{C}$

Soluble in water

$285 \, ^\circ \text{C}, 24 \, \text{h}$

$\text{MSO}_4 \cdot \text{H}_2\text{O} + \text{LiF} \xrightarrow{\text{EMI-TFSI}} \text{LiMSO}_4\text{F}$

Serious contender to $\text{LiFePO}_4$


Fluorosulfates LiMSO$_4$F: a true challenge for theorists

Why different structures depending on M?
DFT + U calculations give little thermodynamic differences; less than $k_B T$...??.

Key challenge ...

Unstable: Decomposes for $T > 320°C$

Make theory more predictive: To reach the point where new compounds together with their properties can be predicted
Towards the eco-efficient elaboration of electrode materials: a few tendencies

Can we make electrode materials at room temperature?

Return to life chemistry

- To develop bio-assisted, bio-inspired or bio-mimetic synthesis approaches to
  - elaborate known or new inorganic materials

Fe₂O₃
From bacteria to electrode materials

**bio-mineralization approach**

Bacillus pasteurii « Urease » kinetically controls urea hydrolysis

\[ \text{Ca} + \text{CO} \rightarrow \text{CaCO} \]

**LiFePO}_4 synthesis**

\[ \text{LiH}_2\text{PO}_4 + \text{H}_2\text{N} + \text{FeSO}_4.7\text{H}_2\text{O} \rightarrow \text{LiFePO}_4 + (\text{NH}_4)_2\text{SO}_4 \]

\[ T = 60^\circ\text{C} \]

8 hours

Collaboration: F. Guyot (Université de Paris VI)
Electrodes from genetically modified viruses

Viruses are used as building blocks, templates

Growth of nano-composite conducting electrodes

Bio-mineralization or virus engineering offers a new approach to design sustainable electrodes

Further inspiration from life chemistry

Inorganic electrodes
Mineral

Possibility of using organic electrodes
Looking for electrochemically active organic electrodes

Get inspiration from the old chemistry on oxocarbons $M_2C_6O_6$ (with $M$ = Li, Na, K, Rb and Cs)

How to make Li$_2$C$_6$O$_6$ from natural resources?

1) $\text{HNO}_3$

2) $\text{O}_2$, Acet. de C

(25% yield)

myo-inositol

Lithium Rhodizonate

From biomass to active electrode

Phytic-acid

Chemical/enzymatic diphosphorylation

8% of the dry weight of corn-steeping liquor

The field of organic chemistry: a fertile domain for sustainable electrodes

Flexibility of the redox potential according to the nature and environment of the electro-active centre
Elaboration of the 1st organic and bio-compatible Li-ion battery ...

- Good thermal stability
- Good cycling behaviour
- Poor performance

Find highly oxidizing Li-based organic electrodes to be used as Li reservoir

$Li_2C_6O_6 \leftrightarrow 2Li^+ + 2e^- + C_6O_6$

$Li_2C_6O_6 \rightarrow 2Li^+ + 2e^- + C0/CO_2$

New concept
- More ecological systems

Main remaining issue ??
### Key numbers:
- 160,000 tons Li₂CO₃ annual production
- 20-25% for battery sector (>32,000 tons)
- Roughly 0.5 kg of Li₂CO₃ per 1kWh battery

### Simple estimation if:
- 10% of the 60 million cars are pure EVs (25 kWh):
- \( \approx 75,000 \) tons: half of today’s total production

### Li Resources (13 M of T)
- **Mineral:**
- **Salars:**
  - Salar de Uyuni (Bolivia): 0.023%
  - Salar de Atacama (Chile): 0.14%
  - Silver peak Nevada: 0.032%
- **See water:** 0.2 ppm

References:
- BEST Spring, 37-41(2009)
- US. Geological survey (2007)
- Under the microscope, MIR (2008)
A few alternatives

To promote recycling

- To develop Li-recovery processes
  - Hydro-metallurgy
  - Simple considerations to produce 1 Ton of Lithium

Post-lithium chemistry: the sodium alternative?

- Higher availability of precursors
  - Na in Earth: $10^3$ ppm
  - Na in Sea: $10^5$ ppm

- Lower performance than Li-ion

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode potential (V)</td>
<td>-3.04</td>
<td>-2.71</td>
</tr>
<tr>
<td>Electrode capacity mAh/g)</td>
<td>3860</td>
<td>1166</td>
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Reincarnation chemistry of materials will become an essential part of future battery business

Potentially cheaper than Lithium chemistry
From Li-ion to Na-ion batteries

Still a material problem

Key Challenge: To find new negative electrode materials?
Increased energy density

Energy = Capacity x Potential

Increased potential V (5 V ?)

Increased capacity (2e⁻ per 3d-metal?)
Thermal vs. Electrical vehicles

How to close the gap between Octane vs. Li-ion?

A factor 15 gap

1 liter of gaz
2300Wh/Kg

1kg of Li-ion
150Wh/Kg

Which chemistries are around the corner ???

(Revisiting Li-S and Metal-air systems and more so the Li-air system)
What are these “attractive” technologies? What can we expect?

**Li-S**

\[ 2\text{Li}^+ + 2e^- + \text{S} \rightleftharpoons \text{Li}_2\text{S} \quad (E^\circ = 2.27 \text{ V}) \]

Energy density = 3802 Wh/kg

Factor of 10 ≈ 380 Wh/kg

≈ 180 Wh/kg

**Li-O₂**

\[ 2\text{Li}^+ + 2e^- + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2 \quad (E^\circ = 3.14 \text{ V}) \]

Energy density = 5259 Wh/kg

Factor of 10 ≈ 500 Wh/kg

≈ 500 Wh/kg

\( \times 3 \)

natural, abundant, cheap feedstock
The Li-oxygen battery

Progresses have been achieved, but major problems remain..

Discharge Reaction:

\[ 2 \text{Li}^+ + 2 \text{e}^- + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2 \]

Shao-Horn – JACS_132_12170_2010:

Collaboration avec P. Bruce: University of St-Andrews, Scotland
Li-air – the numerous challenges

- Anode
  - Inherits problems of Li dendrites

- Cathode
  - To master electrode porosity
  - To reduce the voltage gap

- Electrolyte
  - $O_2$ solubility, diffusivity
  - Master the $O_2^-$ reactivity

Anodes + Cathode + Electrolyte problems → High fading + poor rate capability

Commercial rechargeable Li-air cells have still a long way to go either at the research or applied levels: Be careful …
Mass storage energy (MW): Could Li-ion play a role?

Worldwide Estimated Global installed Capacity energy storage:
1.5% of the consumption

TOTAL: 125,520MW

- Batteries: 451 MW (98%)
- Pumped hydro: 98%

Stationary market will expand

- NaS is stellar
- Li-ion is entering
- Great opportunities for innovative Redox-Flow chemistries
Outlook for Li-ion batteries over the next 20-30 years

Energy density

- Sony 1990
- Sony 1995
- LiMnO₂ 2004
- Nexellon 2005
- Sony 2007
- A123 2015

Conversion Cathodes (nano)

Cathodes organiques

Na-ion chemistry

Li-S

Sustainable development x 2 ou 3

2 MW Li-ion battery

250 Wh/kg, 800 Wh/l

miEV / C0 / Lion

Li-air

Futur e

Futur

Futur

Futur

Futur

Outlook for Li-ion batteries over the next 20-30 years
Conclusions: Beyond scientific challenges...

Research funding worldwide (EVs + Batteries)

**US:** ~9.17b€  **EU:** ~1.2b€  **ASIA:** >3.3b€

- Countries/continents create their own programs, set-up new federative infrastructures
  - Energy Frontiers Research Centers (US)
  - European Network of Excellence (ALISTORE-ERI)
  - French Hub (RS2E) in 2010 reuniting (researchers, engineers, users)

Is it really a problem of money? More a problem of managing/structuring for efficient integration between science and technology

Solving energy issues is a worldwide problem

Find means/tools to foster worldwide cross-sharing information on pre-competitive topics between each national scientific program
Thank you for your attention