Les différentes chimies des batteries lithium-ion et leurs usages industriels

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Energy consumption and demand increase

Equivalent of 10 million of oil barrel consumed since this morning!

TOE = Tons of Oil Equivalent

Renewable energy supply should increase

Increase of energy demand

Clean renewable energy intermittent!

Storage of renewable energy?

Batteries to store energy

from electrical energy
to chemical energy

Increase of energy demand
↓
Clean renewable energy
↓
Storage of renewable energy
↓
Batteries
Energy storage technology: from lead to Li-ion batteries

Specific power (W/kg) = acceleration

Specific energy (Wh/kg) = autonomy

JM Tarascon, Histoire et évolution des technologies d’accumulateurs, Collège de France, 2011
Li-ion market share

Li-Ion Batteries: principle and history

Electrode materials

Safety
Worldwide battery market dominated by lead acid rapid growth of Li-ion batteries

NiMH Nickel Métal-Hydure
NiCd Nickel Cadmium

2004-2014 (CAGR): +16%
NiCd: -2% per year
NiMH: +6 per year
Li-ion: +21% per year

modified from Avicenne Energy, 2014
How does a **battery** work in **discharge**?

**Negative**

\[ \text{LiC}_6 \rightarrow \text{Li}^+ + e^- + C_6 \]

**Positive**

\[ \text{Li}^+ + e^- + \text{CoO}_2 + \rightarrow \text{LiCoO}_2 \]

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when lithium-metal used as negative electrode with liquid electrolyte: formation of lithium dendrite = lithium ‘rod’

Electric short circuit → fire
Li-dendrite issue with Li-metal: 2 solution arose

solution 1

liquid electrolyte $\rightarrow$ polymer

solution 2

Li-metal $\rightarrow$ intercalation material
solution 1

liquid electrolyte → polymer

Li-metal polymer
1978

Limitation of dendrite formation
No organic solvent

Operated at 80°C

Blue Solution Blue Car
2011- présent

Armand, M. B. in Materials for Advanced Batteries, 1980
solution 2

Li-metal $\rightarrow$ intercalation material $\rightarrow$ Li-ion

1983

$= \"rocking chair\"$ battery

$\rightarrow$ 1991, first Li-ion batteries to be commercialized (Sony)

LiCoO$_2$/Graphite
**Li-ion battery history**

1975: Layered structure of LiTiS₂
    - Whittingham

1980: LiCoO₂ (LCO)
    - Goodenough and Mizushima

1983: Graphite as negative LiₓC₆
    - Yazami

1984: LiMn₂O₄ (LMO)
    - Thackeray et al.

1997: LiFePO₄ (LFP)
    - Pahdi, Goodenough

**Solution 1**

- **Li-metal polymer**
  - 1978

**Solution 2**

- **Li-ion**
  - 1983

**Rechargeable Li-metal**
Key requirements for electrode material (theoretical)

Electrochemical properties
possibility to be oxidized/reduced
good electronic conductor

Crystal structure
empty sites to intercalate large amount of Li ion
high lithium chemical diffusion
small volume changing during electrochemical process

Safety – Price
chemically stable, non-toxic, inexpensive
easy to prepare and handling
Li-ion technology: many available positive and negative electrode materials

JM Tarascon, Histoire et évolution des technologies d’accumulateurs, Collège de France, 2011
Substitution in lamellar oxides

from \( \text{LiCoO}_2 \) (LCO) to \( \text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2 \) (NMC)

\[ \text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2 \] (NCA)
Li-ion batteries main application: EVs, light electronic
-» material’s choice depends on its application

LCO, NMC

LMO, LFP, NCA

Source: Avicenne Energy Analyses
Evolution of positive electrode market: LFP quick growth previson

market share in 2015

previsons

LFP LiFePO₄
LMO LiMn₂O₄
NCA LiNi¹⁻y⁻zCoₙAl₂O₂
NMC Li(Ni,Mn,Co)O₂
LCO LiCoO₂

modified from Avicenne Energy Analyses

Asumption: Tesla use NCA and relative success 200 000 EV sold/yr in 2025
Positive electrode price: lithium amount and price is **not so significant** process has to be **optimized**

In a battery: only 2.5 wt.% of Li in a battery, being

$<1g \quad 10g \quad 3.3kg \quad$ of ‘Li-metal’

Metal cost processed in positive electrode ($/kWh) (before cell and pack process yield)

- **LCO** $\text{LiCoO}_2$
- **NMC** $\text{Li(Ni,Mn,Co)}_2\text{O}_2$
- **NCA** $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$
- **LMO** $\text{LiMn}_2\text{O}_4$
- **LFP** $\text{LiFePO}_4$

modified from Fabrice Renard, Oreba 1.0, Montréal, May 2014 and Avicenne Energy Analyses
Anne de Guibert, SAFT Batteries, Matériaux stratégiques pour l’énergie et politiques nationales
Safety

Higher energy density in more powerful Li-ion batteries

- **Tesla model S on fire** – 2016
  - NCA/Graphite

- **Hoverboard after explosion** – 2016
  - LCO-NMC ? /Graphite

- **Boeing 787 Li-battery pack issue** – 2013
  - LCO/Graphite

- **Samsung Galaxy Note 7** – 2016
  - LCO-NMC ? /Graphite

- **Sony laptop** – 2006
  - LCO/Graphite

- **Recycling**
  - 4.3 MILLION SMARTPHONES
Conclusion

The Li-ion technology that will take the lead will have to sacrifice energy density to favour security for a given application.
Perspectives

Rocking chair batteries LTO/LFP: safe, high power to replace **lead acid batteries** in Electric Vehicles

Production of electrode materials with **locally available precursors**

\[ x\text{Li}_2\text{CO}_3 + y\text{TiO}_2 \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} \]

modified from Avicenne Energy Analyses, 2014
K, Zaghib et al., Safe and fast-charging Li-ion battery with long shelf life for power applications, J Power Sources, 196, 8 (2011)
Take a look inside a battery

Batterie 18650

sectional view

Annexes
Production et prix du Lithium aujourd’hui

Production mondiale de lithium

Evolution du prix du Li

http://www.crugroup.com/about-cru/cruinsight/Lithium-The_Problem_With_Prices
Et demain ? 3 scénarios envisagés

- Muted – towards high prices
- Measured stable prices
- Aggressive drastic drop

http://www.crugroup.com/about-cru/cruinsight/Lithium-The_Problem_With_Prices
How much Li we will need in 2020

Cellphone:
2 billions light electronic in 2008 – 1800 tons of Li-metal
w/ 8-10% growth/year : 4500 tons in 2014

10 millions of EV
  > 35 000 tons of Li-metal

10 000 systems pf 1 MWh
  > 1 650 tons of Li-metal

Realistic regarding the reserves, slightly higher than the 37 ktons per year
Réserves mondiales Lithium ≠ Gisement exploités mondiaux !

<table>
<thead>
<tr>
<th>Country</th>
<th>Production</th>
<th>Reserves</th>
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</thead>
<tbody>
<tr>
<td>Argentina</td>
<td>3,800</td>
<td>2,000,000</td>
</tr>
<tr>
<td>Australia</td>
<td>13,400</td>
<td>1,500,000</td>
</tr>
<tr>
<td>Brazil</td>
<td>160</td>
<td>48,000</td>
</tr>
<tr>
<td>Canada (2010)</td>
<td>480</td>
<td>180,000</td>
</tr>
<tr>
<td>Chile</td>
<td>11,700</td>
<td>7,500,000</td>
</tr>
<tr>
<td>People's Republic of China</td>
<td>2,200</td>
<td>3,200,000</td>
</tr>
<tr>
<td>Portugal</td>
<td>300</td>
<td>60,000</td>
</tr>
<tr>
<td>Zimbabwe</td>
<td>900</td>
<td>23,000</td>
</tr>
<tr>
<td>World total</td>
<td>32,500</td>
<td>14,000,000</td>
</tr>
</tbody>
</table>


Et au Québec ?
Salar de Uyuni (Bolivie) – plus grande réserve de sel de lithium

Source : Google - Uyuni et lithium desert
Puissance spé. = accélération

Une batterie se définit par son **voltage** et sa **capacité**

$\Delta E$ (volt)
Différence de potentiel entre électrode négative $-$ et positive $+$

$P (W) = \Delta E (V) \times $ Intensité (A)

$m\text{Ah}/g \rightleftharpoons \text{Capacity} = \frac{26.8 \times dx}{M}$

dx : nombre d’électrons
M: masse molaire (g)

Capacité = Autonomie
Batteries Li-O\textsubscript{2} et Li-S

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{Schematic representations of Li-ion, non-aqueous and aqueous Li-O\textsubscript{2} and Li-S cells.}
\end{figure}

\textbf{Li-O2 and Li-S batteries with high energy storage, Peter G. Bruce et al, Nature Materials, Vol 11, 2012}
Evolution of positive electrode materials production

market share in 2015

previsions

Asumption: Tesla use NCA and relative success 200 000 EV sold/yr in 2025

modified from Avicenne Energy Analyses
Li-ion battery geometries

18650 cell
Source: Cadex

Pouch Cell
=Li-laminate
Source: A123

Button Cell
Source: Sanyo

Prismatic cell
Source: Hitachi

2014 market share

modified from Avicenne, 2014
# Electrode materials limitations

<table>
<thead>
<tr>
<th>Positive</th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>LCO</td>
<td>performance</td>
<td>cost - resource limitations</td>
</tr>
<tr>
<td>NCA</td>
<td>high capacity</td>
<td>safety</td>
</tr>
<tr>
<td>NMC</td>
<td>safety</td>
<td>cost - resource limitations</td>
</tr>
<tr>
<td>LMO</td>
<td>low cost</td>
<td>low capacity</td>
</tr>
<tr>
<td>LFP</td>
<td>excellent safety</td>
<td>limited cycle life</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Negative</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>cycle life</td>
<td>low energy density</td>
</tr>
<tr>
<td>LTO</td>
<td>&quot;zero strain&quot; material</td>
<td>high voltage</td>
</tr>
</tbody>
</table>

- LCO: LiCoO$_2$
- NCA: LiNi$_{1-y-z}$Co$_y$Al$_z$O$_2$
- NMC: Li(Ni,Mn,Co)O$_2$
- LMO: LiMn$_2$O$_4$
- LFP: LiFePO$_4$
- LTO: Li$_4$Ti$_5$O$_{12}$
Utilisation Cathodes par Cathodes dans Applications

Sources: AVICENNE ENERGY Analyses

Thomas Bibienne - Québec Mines - 23 Novembre 2016
Characteristics of the main positive electrode materials

LCO $\text{LiCoO}_2$

NMC $\text{Li(Ni,Mn,Co)}_2\text{O}_2$

LFP $\text{LiFePO}_4$

LMO $\text{LiMn}_2\text{O}_4$

NCA $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$

http://batteryuniversity.com/learn/archive/understanding_lithium_ion
http://batteryuniversity.com/learn/article/types_of_lithium_ion