Battery research for smart mobility: Achievements and new directions

J.M. Tarascon
Battery research is business-driven so are the basic research needs.

Electric mobility: an introduction

Revolution in the word of energy management but also in the way that research must proceed.

100$ / kWh

Specific energy

Cost

Energy efficiency

Power density

95% capacity at 1C

Energy density

No cobalt

Sustainability

100 € kWh\(^{-1}\)

by 2020

Today

2016 2018 2020 2022 2024 2026 2028 2030

Cell Pack

Source: Bloomberg New Energy Finance Scenario 5: Tesla Gigafactory NCA/graphite-Si
The layered oxides and their evolution through the years

- **LiCoO₂ (1991)**
  - CoO₆
  - LiO₆

- **Chemically substituted samples**
  - Replace partially Co by Mn and Ni
  - Li[NiMnCo]O₂
  - NMC phases (170-1900 mAh/g)

- **Stellar "622"**

- **Graph**
  - Voltage (V vs. Li⁺/Li₀)
    - 3.0 to 4.5
  - Capacity (mAh/g)
    - 30 to 150
  - Thermal stability (°C)
    - 200 to 350
  - Capacity Retention (%)
    - 65 to 100
  - X in LiₓCoO₂
    - 0.3 to 0.9

- **Less than 1 Li⁺ exchanged per metal**

- **Improvements via chemical substitutions**
  - Li[Co]O₂ [150 mAh/g]
  - Replace partially Co by Mn and Ni
  - Li[NiMnCo]O₂ [180 mAh/g]
  - NMC phases

Noh et al., J. Power Sources, 2013
T.Ozuku, Y. Makimura; Chem Lett. 642 (2001)
Increasing the capacity further via chemical substitution.

### The Li-rich NMC phases

**Co**

**Ni**

**Mn**

**Li-excess**

\[ \text{Li} \left[ \text{Li}_{0.22} \text{Ni}^{\text{III}}_{0.11} \text{Mn}^{\text{IV}}_{0.54} \text{Co}^{\text{III}}_{0.13} \right] \text{O}_2 \]

### Design model materials

<table>
<thead>
<tr>
<th>3d</th>
<th>4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>Ti</td>
</tr>
<tr>
<td>V</td>
<td>Cr</td>
</tr>
<tr>
<td>Mn</td>
<td>Fe</td>
</tr>
<tr>
<td>Co</td>
<td>Ni</td>
</tr>
<tr>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>Y</td>
<td>Zr</td>
</tr>
<tr>
<td>Nb</td>
<td>Mo</td>
</tr>
<tr>
<td>Tc</td>
<td>Ru</td>
</tr>
<tr>
<td>Rh</td>
<td>Pd</td>
</tr>
<tr>
<td>Ag</td>
<td>Cd</td>
</tr>
</tbody>
</table>

**Li$_2$Ru$^{\text{IV}}_{0.75}$Sn$^{\text{IV}}_{0.25}$O$_3$**

A single cationic redox center

**Capacité identique 250 mAh/g**

**Potentiel (Volts vs. Li$^+$/Li$^0$)**

<table>
<thead>
<tr>
<th>300</th>
<th>240</th>
<th>180</th>
<th>120</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>210</td>
<td>140</td>
<td>70</td>
<td>0</td>
</tr>
</tbody>
</table>

**Capacité en mAh/g 280**

**Voltage (V vs. Li$^+$/Li$^0$)\(x\) in LixRu0.75Sn0.25O3**

**280 mAh/g**

- **Cycle 1**
- **Cycle 2**
- **Cycle 3**
- **Cycle 10**

**280 mAh/g**
Origin of the extra capacity in Li-rich materials

Direct evidence for an anionic redox process $(2O^- \rightarrow (O_2)^{n-})$ in Li-rich lamellar compounds.

M. Sathya, J.M. Tarascon et al. (Nature communications, Fevrier 2015)
The anionic redox activity: a transformational change

LIB has relied on cationic redox reactions

(2D Layered oxide)

Cationic framework

Anionic framework

NATURE MATERIALS, 2013, 12, 827-835

150 mAh/g
A new playground for designing high capacity electrodes

**Structural dimensionality**
- **3D**
- **2D**
- **1D**
- **0D**

**Li/M composition**

- **3D**
  - Li$_{1.3}$Nb$_{0.3}$Me$_{0.4}$O$_2$ (Me = Mn, Fe,)
  - Cation-disordered Rock-salts
- **2D**
  - Layered Li-rich NMC
- **1D**
  - Ru chain-ordering in Li$_3$RuO$_4$
- **0D**
  - Nb$_4$O$_{16}$ clusters in Li$_3$NbO$_4$

**Local Structure**
- Increasing the number of O Non-Bonding States
  - Li$^2$M$^4+$O$^3$ Li$^3$M$^5+$O$^4$

**Layered Li-rich NMC**
- α-Li$_2$IrO$_3$ (isostructural with Li$_2$MnO$_3$ or Li$_2$RuO$_3$)

**Tridimensional ordered β-Li$_2$IrO$_3$**
- Layered Li$_3$IrO$_4$

**Cation-disordered Rock-salts**
- Li/M composition

**Not exist...**

Layered LiMO$_2$ oxides have enabled today’s boom in EV’s.

Is it the perfect solution with respect to sustainability?

- Energy needed $\approx 327$ kWh
- CO$_2$ rejected $\approx 110$ kg

**Life cycle analysis**

Ishihara, K. et al. Life Cycle Analysis
How to make more sustainable Li-ion batteries? A few trends

- Design electrode materials based on abundant chemical elements
- Develop energy-saving synthesis routes
- Use of renewable organic electrodes
- Explore chemistries beyond Li

**Sustainability thrust:** diversification of the battery systems for enhanced performances

None have reached the maturation stage ...
The Na-ion battery: an alternative to Li-ion for sustainability

<table>
<thead>
<tr>
<th>Name</th>
<th>Earth abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogène</td>
<td>0.88 %</td>
</tr>
<tr>
<td>Lithium</td>
<td>0.006 % 0.006%</td>
</tr>
<tr>
<td>Béryllium</td>
<td>0.0003 %</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.6 % 2.6%</td>
</tr>
</tbody>
</table>

Earth abundance

\[ \text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3 \parallel \text{NaPF}_6 \text{ in PC/EC/DMC} \parallel \text{C} \]

Cell potential (V)

Capacity in mAh/g of NVPF

Need of an extra Na source..

Oversodiated materials (\( \text{Na}_{3+x}\text{V}_2(\text{PO}_4)_2\text{F}_3 \))
How to prepare a Na-rich phase via a sustainable approach?

**Synthesis via ball milling**

\[
Na_3V_2(PO_4)_2F_3 + Na
\]

Milling time = 2 hours

"Na\(_{3+x}\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\) composite (3<x<4)"

**Electrochemical performance**

\[
Na_4V_2(PO_4)_2F_3 \quad \text{(New phase)}
\]

Assembly of 18650 Na-ion cells for benchmarking against Li-ion


The Na$_3$V$_2$(PO$_4$)$_2$F$_3$/C technology: First 18650 prototypes

4000 cycles

Cycle life of Na-ion cells at 1C

Power rate of C/NVPF Na-ion cells

Poor 55°C cycling and self-discharge performances
The Na$_3$V$_2$(PO$_4$)$_2$F$_3$/C technology: 55°C cycling & self discharge

**Cycle life & One week self-discharge of NVPF/C at 55°C**

- 105Wh/kg ~ 3000 cycles
- 80% at 10C
- 55°C storage

**New electrolyte formulation**

- 11th
- 15th
- 20th

**Capacity (mAh g$^{-1}$) based on NVPF mass**

**Cell voltage (V)**

**Capacity retention (%)**

55°C at C/10
What could be tomorrow’s battery research

Basic problems emerging from concrete technological challenges
Looking ahead: New research challenges

Business players change today’s traditions

Cost per kWh of stored energy = \[\text{Chemistry/Material performance} + \text{Volume production} + \text{Battery second life}\]

Better traceability

Establish the state of health record of the battery just like for humans

E. Musk: (100 $ kWh in 2025)

Efforts towards instrumental miniaturization for real time monitoring of the batteries in the field

Interdisciplinary research which is still in its embryonic state

Establish the state of health record of the battery just like for humans

Electrode recovered by an SEI
(Prevents the crossing of Li\(^+\))

Build self-healing processes into the original battery design (vectorization)

Clogged artera by cholesterol
(Prevents blood circulation)

Develop self-healing processes

Looking ahead: New research challenges

How to tackle this issue?
Innovative chemistry on the battery separator

- Multilayers
- Surface-functionalization
- External or internal stimulation
  - Encapsulated self-healing molecules

**Functionabilization to trap species released from side reactions**

- Functionalization with \(\mathrm{SO}_3^-\)-Nafion groups
- Fluorinated graphene oxide
Electric mobility: Conclusions

Anionic redox as a new paradigm to design electrodes with double capacities

Li-ion batteries with ~ 20% energy density improvements

Future research challenges dealing with SOH batteries
Development of sensing and self-healing processes via innovative chemistry

Development of a C/Na₃V₂(PO₄)₂F₃ Na-ion technology via materials and electrolytes innovations
Na-ion batteries with attractive power rate performances

Foreseen EV future

Hardware
Software + services

Foreseen battery future
Materials Sensing + monitoring)
Thank you for your attention

http://www.college-de-france.fr/site/en-college/index.htm