Advanced electrode materials for Na-ion batteries. An emerging technology
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www.cicenergigune.com

What is the CIC energigune?

- CIC energigune, founded in 2007, is a **new Cooperative Energy Research Centre**, located in the Basque Country of Spain.

The Basque Country is renowned for the beauty of its natural surroundings. It offers high standards of living and quality of life, in terms of health, housing, leisure, sports, etc, making it an attractive area to live in.
Introduction

Targets on Na-ion battery technologies

Anode materials
- Hard Carbon
- Poly-Schiff bases
- Carbodimides

Cathode materials
- Sodium-vanadium fluorophosphates
- Sodium Layered Oxides

Conclusions
To satisfy the industrial needs developing of new batteries is required:

- **High energy density batteries**: Metal-oxygen/air batteries
- **Low cost batteries**: Sodium-ion batteries.
- **Other types of batteries that have attracted much attention**: Magnesium-ion
  Organic electrode batteries

Na-Based batteries

Sodium ion non aqueous → Sodium ion aqueous → Sodium sulfur HT → ZEBRA HT → Sodium Air

R&D/Demo → Demo → Commercial → R&D

Na ion non aq.
- Low Cost
- High Power
- High voltage among other Na systems

Low Temp Na - S
- Low Cost System
- Low Operating cost
- High Energy
- Safety
- Established Engineering

Scale Up of Materials For Prototypes !!!!
Sodium-ion batteries

Na-based cells have difficulties competing with Li based cells because of energy density considerations.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Na</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Price (for carbonates) (€/kg)</td>
<td>0.07-0.37&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.11-4.49&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Capacity density (Ah/g)</td>
<td>1.16</td>
<td>3.86</td>
</tr>
<tr>
<td>Voltage vs. S.H.E.</td>
<td>-2.7</td>
<td>-3.0</td>
</tr>
<tr>
<td>Ionic radius (Å)</td>
<td>0.98</td>
<td>0.69</td>
</tr>
<tr>
<td>Melting point (° C)</td>
<td>97.7</td>
<td>180.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Purity: 98.8-99.2% min.
<sup>b</sup> Battery grade: 99.9%.

 Aluminium can be used as current collector (negative electrode).
No Na-Al alloy formation (Li-Al alloys form)!
- Al is lighter and inexpensive than Cu.
- CO₂ signature of Al much lower compared to Cu.

Na forms many more potentially interesting compounds compared to Li. (Pearson concept)

Very soft Mechanical stability:
Dendrite formation might be more effectively prevented by mechanical pressure than is the case for Li.

Transport and charge transfer of Na⁺ in liquid and polymer electrolytes is often easier compared to Li⁺ due to lower solvation enthalpy. (Na ions polarise their environment less).

Na-ion cells would be appropriate for applications such as storage of off-peak and essentially fluctuating renewable energies, such as wind and solar farms.
Schematic of a typical Na-ion cell

Na$_{2/3}$MO$_2 \rightarrow$Na$_{2/3-x}$MO$_2 + x$Na$^+ + xe^-$

1M NaPF$_6$

EC:DMC

Na$_2$Ti$_3$O$_7 + 2$Na$^+ + 2e^- \rightarrow$Na$_4$Ti$_3$O$_7$

Ideal Battery:
- High cell voltage and specific capacity
- High energy density
- Safety
- Low cost
- Long cycle life.
Targets of Na-ion battery technology

- **Modeling Calculations:**
  - **Energy Density:** 210 Wh/kg
    - Cathode capacity of 200 mAh/g
    - Anode: 500 mAh/g
    - Average Cell Potential: 3.3V

- **Development of ~ 10 kWh storage unit:**
  - To sustain more than > 5000 cycles with high energy density
  - Specific capacity ~ 150-200 mAh/g (this target may change as per actual voltage of the cell).
  - <10% capacity degradation (current standard is > 20%).
  - Green and ecologically sustainable material for Na-ion battery.
  - Low capital and Low product costs.
  - Ensuring reliability of the complete system.
Anode Materials for Na-ion batteries

Cathode Materials for Na-ion batteries

Energy density (Wh/Kg)

Most common materials for Li-ion batteries
Current research of Na-ion electrode materials at CIC

**cathodes**
- Fluorophosphates
- Layered oxides

**anodes**
- Hard Carbon
- Poly-schiff
- Carbodiimides

![Graph showing electrochemical performance of various materials](image)
Carbon anodes from industrial wastes

Anode materials

First cycles:

NaClO₄ 1M EC:PC 0.002-2V

Key performance indicators:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Synth. Tº</th>
<th>Cycling at 25mA/g</th>
<th>Cycling at 372 mA/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>initial Q (mAh/g)</td>
<td>80% initial Q cycle nº</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>reversible</td>
<td>irrevers.</td>
</tr>
<tr>
<td>Hard carbon 1</td>
<td>sugar</td>
<td>1050ºC</td>
<td>285</td>
<td>96</td>
</tr>
<tr>
<td>Hard carbon 2</td>
<td>Industrial waste</td>
<td>900ºC</td>
<td>254</td>
<td>145</td>
</tr>
<tr>
<td>Soft carbon</td>
<td>Industrial waste</td>
<td>800ºC</td>
<td>165</td>
<td>55</td>
</tr>
</tbody>
</table>

State of the art performance of sugar hard carbon (our reference)

Promising reversible capacity of hard carbon from waste (254 mAh/g)

Promising high rate capacity of soft carbon from waste

Development of carbons from industrial waste precursors with synthesis below 1000ºC (low cost, sustainability, green)
Anode materials

- Organic electrode (Poly-Schiff bases) as anodes vs Na

- Low hysteresis
- Stable capacity in powder electrode
- High capacity retention
- Stable cycle life.
- Carbon optimization yields 350 mA h/g (2.8 Na⁺ ions per monomer unit)

E. Castillo et al, Angew. Chem. 2104, 126, 1-6
Anode materials

**Carbodiimides**

\[
\begin{align*}
\text{MCl}_2 + \text{H}_2\text{NCN} + \text{NH}_3 & \rightarrow \text{MNCN} + 2 \text{HCl} + \text{NH}_3 & (M= \text{Cu, Zn}) \\
\text{MnCl}_2 + \text{Li}_2\text{NCN} & \rightarrow \text{MnNCN} + 2 \text{LiCl} & \text{at R.T} \\
\text{MCl}_2 + \text{H}_2\text{NCN} + \text{NH}_3 & \rightarrow \text{M(HNCN)}_2 + 2 \text{HCl} + \text{NH}_3 & (M= \text{Fe, Co, Ni}) \\
\text{MCl}_2 + \text{H}_2\text{NCN} + \text{NH}_3 & \rightarrow \text{LiCl}/\text{KCl} & \text{at } 370^\circ\text{C} \\
\end{align*}
\]

- TM carbodiimides are shown electrochemically active for Na-ion batteries for the first time
- Improvement of the electrochemical performance in terms of energy density and efficiency vs. oxides
- High capacity values for CoNCN and NiNCN in the first cycles (~800 mAh/g)
- FeNCN less polarization and 1\textsuperscript{st} cycle irreversible capacity.
- In situ XRD measurements show a conversion reaction for CuNCN

Current research of Na-ion electrode materials at CIC

**cathodes**
- Fluorophosphates
- Layered oxides

**anodes**
- Hard Carbon
- Poly-schiff
- Carbodiimides

![Graph showing various Na-ion electrode materials with their corresponding Ewe vs. Na/Na+ (V) and capacity (mAh/g) data.](image)
Cathode materials

- Sodium-vanadium fluorophosphates $\text{Na}_3\text{V}_2\text{O}_{2x}\text{(PO}_4\text{)}_2\text{F}_{3-2x}$

- Theoretical specific capacity of $130 \text{ mAh} \cdot \text{g}^{-1}$ for $\text{Na}_3\text{V}_2\text{O}_2\text{(PO}_4\text{)}_2\text{F}$

- Theoretical specific capacity of $128 \text{ mAh} \cdot \text{g}^{-1}$ for $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$

- Isostructural compounds ($\text{P4}_2/\text{mnm}$).

- $\text{Na}_3\text{V}_2\text{O}_{2x}\text{(PO}_4\text{)}_2\text{F}_{3-2x}$ exhibits two crystallographic F atoms. One F is replaced by O.

- There are two Crystallographic Na$^+$ cations in the structure

Cathode materials

\[ \text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_{2}\text{F}_{3-2x} \]

\[ X = 0.8 \]

6.4 wt. % C

\( \text{V}^+3.8 \)

\[ \text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F} \]

\[ X = 1 \]

0 wt. % C

\( \text{V}^+4 \)

\[ \text{F}_2\text{O} \]

\[ \text{O} \]

- **Specific capacity** (≈ 100 mAh·g\(^{-1}\)) near to theoretical one
- 3.6 and 4.1 V vs. Na/Na\(^+\) → **high energy density**
- **Excellent ciclability** (up to 200 cycles at 1C)
- 95% of capacity retention and a culombic efficiency> 99% after 200 cycles at 1C.

Better performance with carbon coating (≈ 4wt.%C)

**Theoretical specific capacity**

128-130 mAh·g\(^{-1}\)

**Theoretical specific capacity**

130 mAh·g\(^{-1}\)

- 3.6 and 4.0 V vs. Na/Na\(^+\) → **high energy density**
- **novel single-step** hydrothermal synthesis
- Carbon coating - improvement of electrochemical behaviour: 91 mAh·g\(^{-1}\) vs. 102 mAh·g\(^{-1}\) at C/20
- **Ex situ XAS measurements**: \( \text{V}^+4 / \text{V}^+5 \) evolution

Serras et al. J.Power Sources, 2013, 241, 56-60

Cathode materials

- **Na$_3$V$_2$O$_{2x}$(PO$_4$)$_2$F$_{3-2x}$**: Electrochemical mechanism by In-situ Synchrotron XRD

How do the MV and V4 materials react to overcharge up to 4.8 V vs Na/Na$^+$?

**MV**

At 4.8 V: Na$_{0.508(12)}$V$_2$O$_{1.6}$(PO$_4$)$_2$F$_{1.4}$

Preference for Na(2)

V $^+$5 → Maximum $C_{sp}$ reached

**V4**

At 4.8 V: Na$_{1.21(10)}$V$_2$O$_2$(PO$_4$)$_2$F

Preference for Na(1)

V $\sim$ +4.90 → Similar to charge up to 4.3 V, no extra $C_{sp}$

<table>
<thead>
<tr>
<th></th>
<th>V$^{3.8+}$</th>
<th>V$^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3 V normal charge</td>
<td>Na content = 0.77(4)</td>
<td>Na content = 1.24(13)</td>
</tr>
<tr>
<td>4.8 V Overcharge</td>
<td>Na content = 0.508(12)</td>
<td>Na content = 1.21(10)</td>
</tr>
</tbody>
</table>

Cathode materials

- \( \text{Na}_3 \text{V}_2 \text{O}_{2x} (\text{PO}_4)_2 \text{F}_{3-2x} \): Electrochemical mechanism by In-situ Synchrotron XRD

How do the MV and V4 materials react to overcharge up to 4.8 V vs Na/Na⁺?

At 4.8 V: \( \text{Na}_{0.508(12)} \text{V}_{2} \text{O}_{1.6} (\text{PO}_4)_2 \text{F}_{1.4} \)

Preference for \( \text{Na}(2) \)

\( V +5 \quad \text{Maximum } C_{\text{sp}} \text{ reached} \)

At 4.8 V: \( \text{Na}_{1.21(10)} \text{V}_2 \text{O}_2 (\text{PO}_4)_2 \text{F} \)

Preference for \( \text{Na}(1) \)

\( V \sim +4.90 \quad \text{Similar to charge up to 4.3 V, no extra } C_{\text{sp}} \)

How is the structural stress affected by pushing up to its limit in each normal charge?

Low structural stress:
- monophasic after overcharge,
- no significant diff. maxima broadening
- crystallinity preserved

High structural stress:
- phase segregation
- diff. maxima broadening
- crystallinity loss

More FLEXIBLE structure: Better electroch. performance

The letter indicates the environment where Na is located:
(O: octahedral and P: prismatic).

The number indicates the number of unique interlayers that are surrounded by different oxide layers.

The use of prime(´) indicates a distorted phase.
Sodium Layered Oxides as cathodes

- Large initial reversible capacity
- Low polarization \([1,2]\)

**Na-Mn-O**

- Dissolution in electrolyte\([3]\)
- Rapid capacity fade: Jahn-Teller high spin Mn\(^{3+}\) \((t_{2g}^{3}e_{g}^{1})\)\([4]\)

**Na-Mn-Fe-O**

- Higher average voltage
- Environmental friendly TM
- Cell polarization
- Phase transition upon cycling

\(\text{Na}_{x}\text{Mn}_{y}\text{Fe}_{1-y}\text{O}_2\)

\(x \approx 0.7 \rightarrow \text{P2 type} \quad \text{and} \quad 0.7 < x \leq 1 \rightarrow \text{O3 type}\)

**Na-Mn-Fe-Ti-O**

- Stable cycling performance at high C rates
- Loss of a small amount of energy density (capacity of active redox couple)

\(\text{Na}_{0.67}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Ti}_{0.1}\text{O}_2\)

**Na-Mn-Mg-O**

- Increase the structural stability with Mg content
- Decrease in polarization

\(\text{Na}_{0.67}\text{Mn}_{1-x}\text{Mg}_x\text{O}_2\)

**Na-Mn-M-Mg-O**

- Preliminary results
- Average operating voltage: > 3.0 V
- Excellent capacity retention

\(\text{Na}_{0.67}\text{Mn}_{0.7}\text{M}_y\text{Mg}_x\text{O}_2\)

\(x \approx 0.7 \rightarrow \text{P2 type} \quad \text{and} \quad 0.7 < x \leq 1 \rightarrow \text{O3 type}\)
Sodium Layered Oxides as cathodes

Synthesis of P2 and O3 phases with same stoichiometry under different conditions

**P2-** Na$_{2/3}$Mn$_{1/3}$Fe$_{2/3}$O$_2$

**O3-** Na$_{2/3}$Mn$_{1/3}$Fe$_{2/3}$O$_2$

Successful synthesis of pure P2 and O3-phases Na$_{2/3}$Mn$_{1/3}$Fe$_{2/3}$O$_2$

Electrochemical behaviour

The electrochemical performance of this phase does not depend on the layer stacking sequence

Sodium Layered Oxides as cathodes

\[ \text{Na}_{0.67}\text{Mn}_{0.8}\text{Fe}_{0.1}\text{Ti}_{0.1}\text{O}_2 \]

Synthesized by solid state reaction of the oxides.

Cell parameters: \( a = 2.9143(2) \, \text{Å} \), \( c = 11.184(1) \, \text{Å} \)

**Electrochemical performance**

- 2\(^{nd}\) charge/discharge capacity of 146.57/144.16 mAh\(^{-1}\) (0.58 Na\(^+\)) at C/10
- Average voltage: 2.77 V
- 95.09 % Capacity retention (98 % Coulombic efficiency)

- Excellent electrochemical response at 1C for 300 cycles:
  - 87.17 mAh\(^{-1}\) at the 300\(^{th}\) cycle (87.70% capacity retention)

M. H. Han *et al.* Patent EP15382165
Sodium Layered Oxides as cathodes

Na-Mn-Mg-O  Effect of Mg doping

Stability of the host structure: Na$_{0.67}$Mn$_{1-x}$Mg$_x$O$_2$

1. Structural stability increase
2. Suppression of average voltage
3. Decrease in polarization

J. Billaud et al., *Energy and Environ. Science* 2014, 7, 1387
Sodium Layered Oxides as cathodes

Na-Mn-Mg-O

Na$_{0.67}$Mn$_{0.8}$Mg$_{0.2}$O$_2$: Electrochemical mechanism by \textit{In-situ} XRD

- 002 reflection
- 110 reflection
- 1/3,1/3,0 (Mn/Mg ordering)

Phase evolution predominantly solid solution

Mg/Mn ordering does not change during cycling

Evolution during battery function:
- Na extraction occurs first from Na(2) followed by Na(1).
- Na insertion occurs first to the Na(1) site.
- Na does not re-insert or transfer to Na(2) on charge.

- Na$^+$ site occupancies in the layered structures are exchangeable and fluent.
- High mobility of the Na$^+$ ions.

\textbf{EXCELENT CANDIDATES FOR CATHODES IN SODIUM-ION BATTERIES.}

Faradion demonstrates proof-of-concept sodium-ion electric bike

3Ah pouch cell
Layered oxides based cathodes/hard carbon anode

http://www.faradion.co.uk/technology/sodium-ion-technology/

A new prototype battery

French team

Features:
- Battery using sodium ions in the usual “18650” (1.8 x 6.5 cm) format
- The energy density performance (90Wh/kg)
- Excellent cycle life (at least 2,000 charge/discharge cycles)

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