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IDEAS THAT WORK
8-9 October 2015 | CSIR ICC

Research and development of advanced batteries and supercapacitors at the CSIR

Kenneth I. Ozoemena

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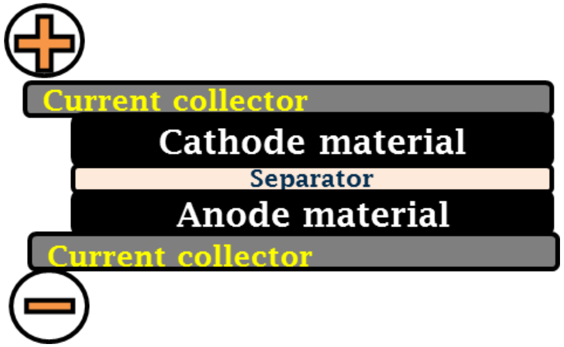
CELEBRATING 70 Years
Ideas that work

Presentation Outline

- Battery vs Supercapacitors
- General applications
- Grid-scale applications (lower hanging fruits)
- CSIR RD&I strategy
- Value-addition to local raw materials

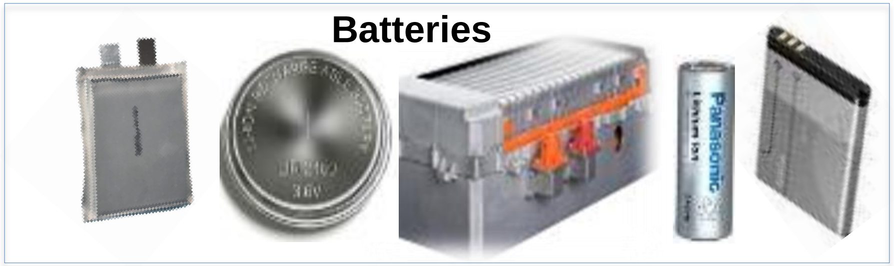
Battery (Energy) vs. Supercapacitor (Power)



World champion in the **10,000 metres**

World champion in the **100 metres**

Long distance = Energy



Speed = Power

- Described as ‘batteries on steroid’
- Burst of energy when needed

Source: Wikipedia images

Different shapes and sizes for several applications

Residential/Commercial/Utility/Power

Portable Electronics

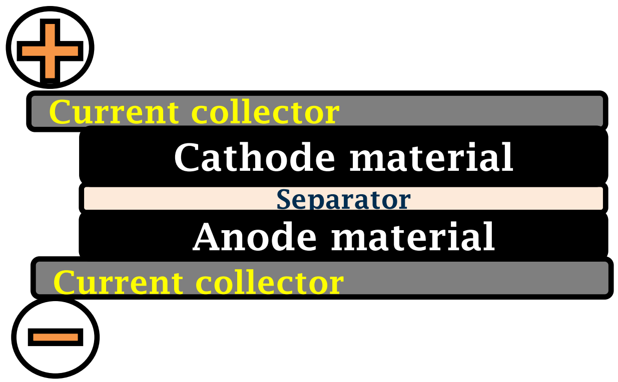
Automotive

Industrial Equipment

Source: Wikipedia images

Grid-scale applications

- Price arbitrage
- Peak-shaving
- Frequency regulation
- Island and off-grid storage
- T&D upgrade deferral
- Voltage-control



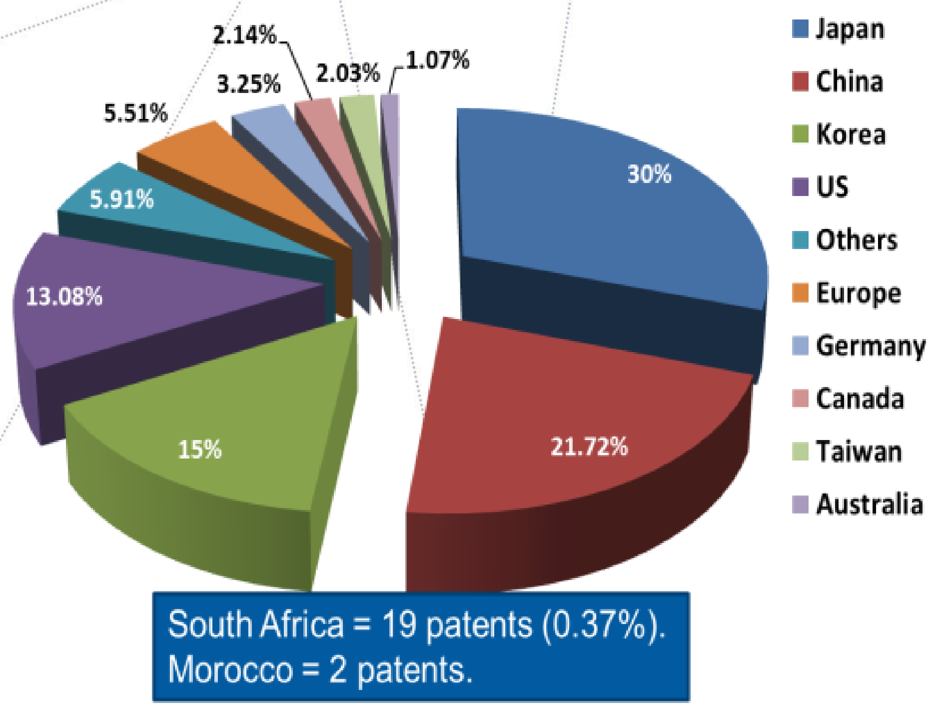
Motivation for our R&D

World Ranking	Critical mineral resources in SA for energy storage
1	Manganese
1	Vanadium
1	Titanium
1	Chromium
2	Ruthenium
2	Zirconium
2&3	Fluorspar / Fluorite

Motivation cont'd:

But…where is Africa

Geographical distribution of lithium-ion battery patents based on publications (1970 – 2010)



Source: KI Ozoemena analysis

Motivation Cont'd

- ✓ ***"The development opportunity of smart(er) grids and storage solutions – which can help in integrating variable renewable technologies – should also be considered…" (IRP, p.21).***

- ✓ ***"…an expanded renewable energy programme; an effective mix of energy efficiency…; investments in an efficient public transport system" (NDP, p.180)***

- ✓ ***"South Africa has a systemic shortage of skills and capacity. The transition to low-carbon economy depends on the country's ability to improve skills in the workforce" (NDP, p.181).***

RD&I Strategy

Solving critical global problems

"Quadruple Combination Processes (QCP)"

* ***Doping*** *(with cations and/or anions)*
  - *Structural stabilisation*
* ***Nano-sizing:***
  - *Enhanced mass transport*
* ***Surface-coating:***
  - *Structural stabilisation,*
* ***Microwave irradiation:***
  - *Enhanced electrochemstry*

Typical manganese-based cathode materials

Spinel materials (Thackeray et al.)

$LiM_xMn_{2-x}O_4$ (M = cations)

- ✓ $LiMn_{1.5}Ni_{0.5}O_4$ **(LMNO)**
- ✓ $LiMn_2O_4$ **(LMO)**
- ✓ $LiAl_{0.3}Mn_{1.7}O_4$ **(LMOA)**

Layered materials (Thackeray et al.)

$xLi_2MnO_3.(1-x)\ LiMO_2$ (M= cations)

- ✓ $L_i[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ **(NMC)**
- ✓ $L_i[Li_{0.2}Mn_{0.52}Ni_{0.13}Co_{0.13}Al_{0.02}]O_2$ **(NMCA)**

Olivine materials

$LiM_xFe_{1-x}PO_4$ (M = Cations):

- ✓ $LiFe_{0.8}Mn_{0.2}PO_4$ **(LFMP)**

Sodium-ion cathode materials

$Na_{2/3}[M_xMn_{1-x}]O_2$ (M= Al, Mg)

- ✓ $Na_{0.67}[Mn_{0.72}Mg_{0.28}]O_2$ **(SMO)**
- ✓ $Na_{0.67}[Mn_{0.72}Mg_{0.28}]O_{1.98}F_{0.02}$ **(SMOF)**

Patent applications in some of them

$LiMn_2O_4$

Challenges:

Capacity fading with time..@ high temperatures

- Disproportionation reaction
- Jahn-Teller effect

RSC Advances

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Microwave-assisted optimization of the manganese redox states for enhanced capacity and capacity retention of $LiAl_xMn_{2-x}O_4$ ($x = 0$ and 0.3) spinel materials†

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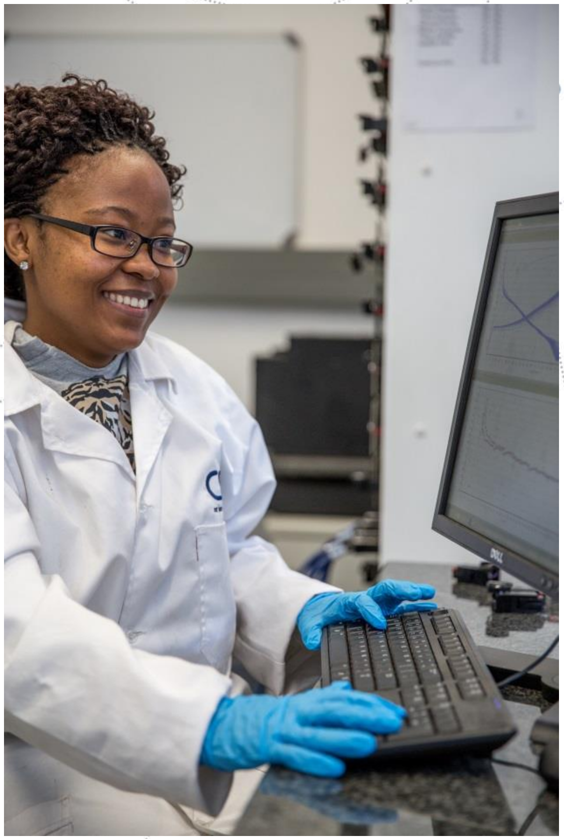
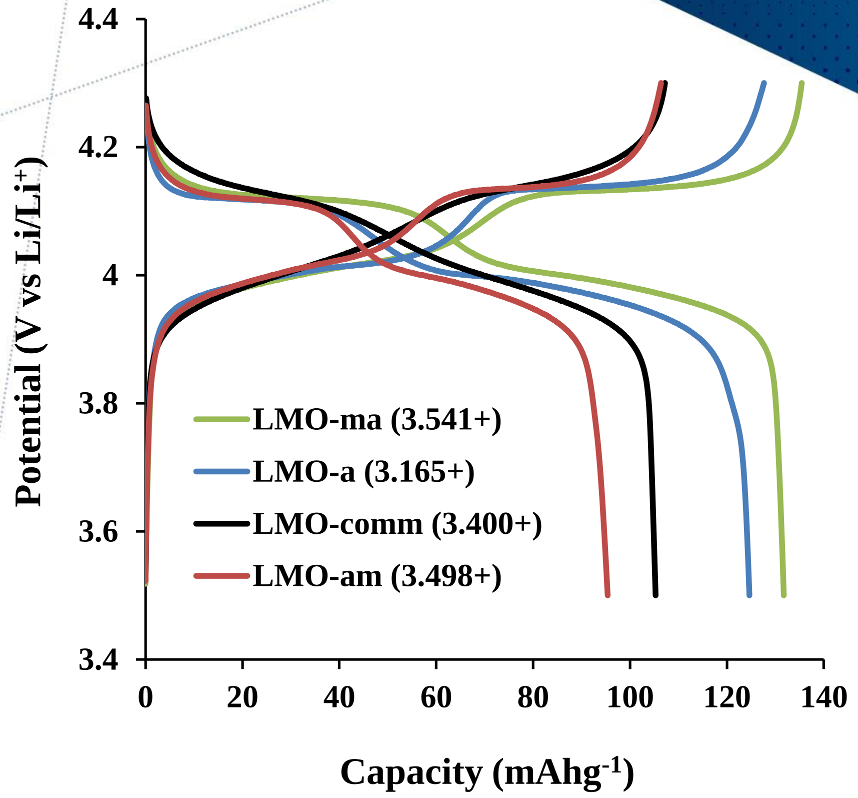
www.rsc.org/advances

Microwave irradiation at the pre- and post-annealing steps of the synthesis of $LiAl_xMn_{2-x}O_4$ ($x = 0$ and 0.3) spinel cathode materials for rechargeable lithium ion batteries is a useful strategy to optimize the average manganese valence number (n_{Mn}) for enhanced capacity and capacity retention. The strategy impacts on the lattice parameter, average manganese valence, particle size and morphology, reversibility of the de-intercalation/intercalation processes, and capacity retention upon continuous cycling. Microwave irradiation is able to shrink the particles for improved crystallinity. The XPS data clearly suggest that microwave irradiation can be used to tune the manganese valence (n_{Mn}), and that the $LiAl_xMn_{2-x}O_4$ with $n_{Mn} \approx 3.5+$ gives the best electrochemical performance. These new findings promise to revolutionize how we use microwave irradiation in the preparation of energy materials and various other materials for energy storage and conversion materials for enhanced performance.

Battery Testing





High-voltage $LiMn_{1.5}Ni_{0.5}O_4$

Challenges:

- Difficulty to obtain pure materials
- Controlling the Mn^{3+} content
- Marching / appropriate electrolytes

ACS APPLIED MATERIALS & INTERFACES
Research Article
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Microwave-Assisted Synthesis of High-Voltage Nanostructured $LiMn_{1.5}Ni_{0.5}O_4$ Spinel: Tuning the Mn^{3+} Content and Electrochemical Performance

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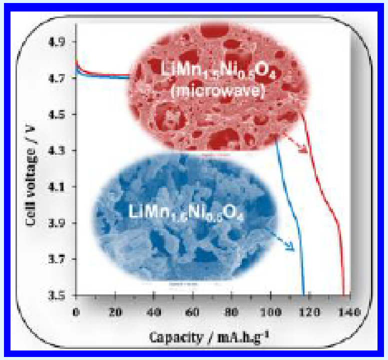
Supporting Information

ABSTRACT: The $LiMn_{1.5}Ni_{0.5}O_4$ spinel is an important lithium ion battery cathode material that has continued to receive major research attention because of its high operating voltage (~4.8 V). This study interrogates the impact of microwave irradiation on the Mn^{3+} concentration and electrochemistry of the $LiMn_{1.5}Ni_{0.5}O_4$ spinel. It is shown that microwave is capable of tuning the Mn^{3+} content of the spinel for enhanced electrochemical performance (high capacity, high capacity retention, excellent rate capability, and fast Li^+ insertion/extraction kinetics). This finding promises to revolutionize the application of microwave irradiation for improved performance of the $LiMn_{1.5}Ni_{0.5}O_4$ spinel, especially in high rate applications.



KEYWORDS: *$LiMn_{1.5}Ni_{0.5}O_4$, Pechini method, microwave irradiation, Mn^{3+} concentration, XPS, electrochemistry*

Patent (PCT) application and scale-up production in progress

Li-and Mn-rich layered oxide materials

$xLi_2MnO_3 \cdot (1\text{-}x)\ LiMO_2$

(where M= transition metal)

Thackeray et al, 1991

For example, $\mathbf{0.5Li_2MnO_3 \cdot 0.5LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2}$

aka: $\mathbf{Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2}$

Challenges

- Low initial Coulombic efficiency
- Rate capability
- Voltage decay (cycle stability)

Some new findings on Mn-based materials

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0013-4651/2015/162(4)/A768/6/$33.00 © The Electrochemical Society

Microwave Irradiation Controls the Manganese Oxidation States of Nanostructured ($Li[Li_{0.2}Mn_{0.52}Ni_{0.13}Co_{0.13}Al_{0.02}]O_2$) Layered Cathode Materials for High-Performance Lithium Ion Batteries

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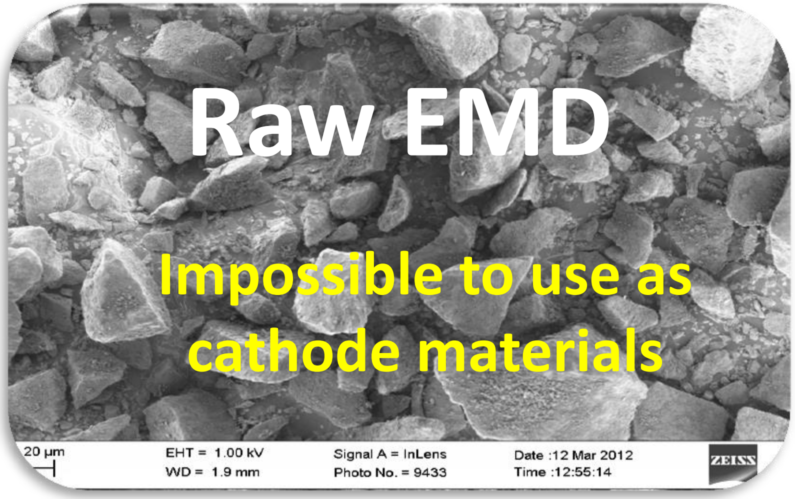
A hybrid synthesis procedure, combining microwave irradiation and conventional annealing process, is described for the preparation of lithium-rich manganese-rich cathode materials, $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ (LMNC) and its aluminum-doped counterpart, $Li[Li_{0.2}Mn_{0.52}Ni_{0.13}Co_{0.13}Al_{0.02}]O_2$ (LMNCA). Essentially, this study interrogates the structure and electrochemistry of these layered cathode materials when subjected to microwave irradiation (these microwave-based produced are abbreviated herein as $LMNC_{\text{-mic}}$ and $LMNCA_{\text{-mic}}$). The nanoparticulate nature of these layered cathode materials were confirmed by SEM. The crystallinity and layeredness were determined from the XRD analysis. The XPS measurements proved a definite change in the oxidation states of the manganese due to microwave irradiation. The galvanostatic charge-discharge characterization showed that the aluminum-doped cathode material obtained with the assistance of microwave irradiation has superior electrochemical properties. In summary, the electrochemical performance of these cathode materials produced with and without the assistance of microwave irradiation decreased as follows: $LMNCA_{mic}$ > LMNCA > $LMNC_{mic}$ > LMNC.

RSA patent application in progress

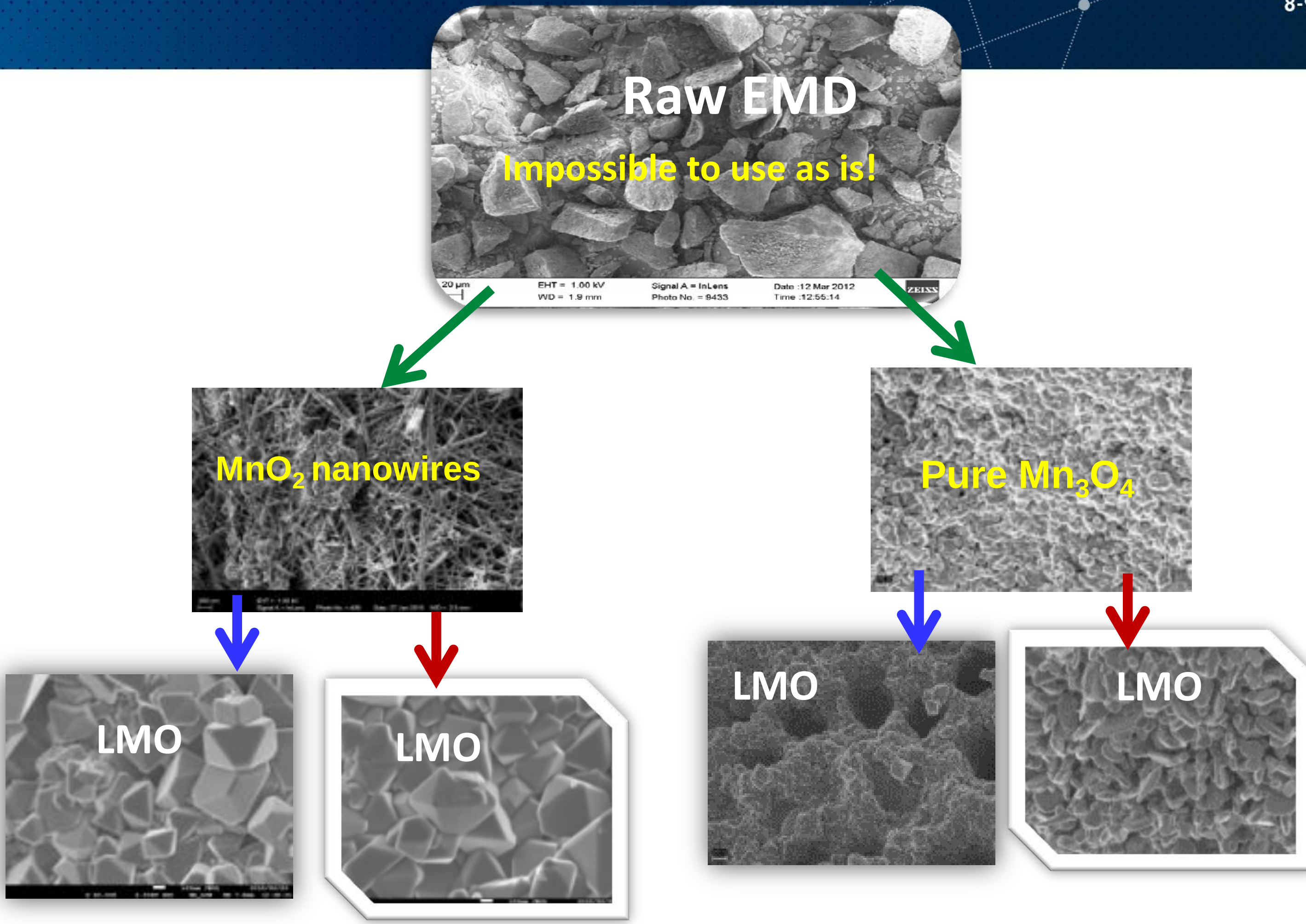
VALUE-ADDITION

Converting local raw electrolytic manganese dioxide (EMD) to useful precursor materials for:

- Lithium-ion batteries
- Sodium-ion batteries
- Supercapacitors
- Electrocatalysts for
    - ✓ metal-air batteries
    - ✓ fuel cells

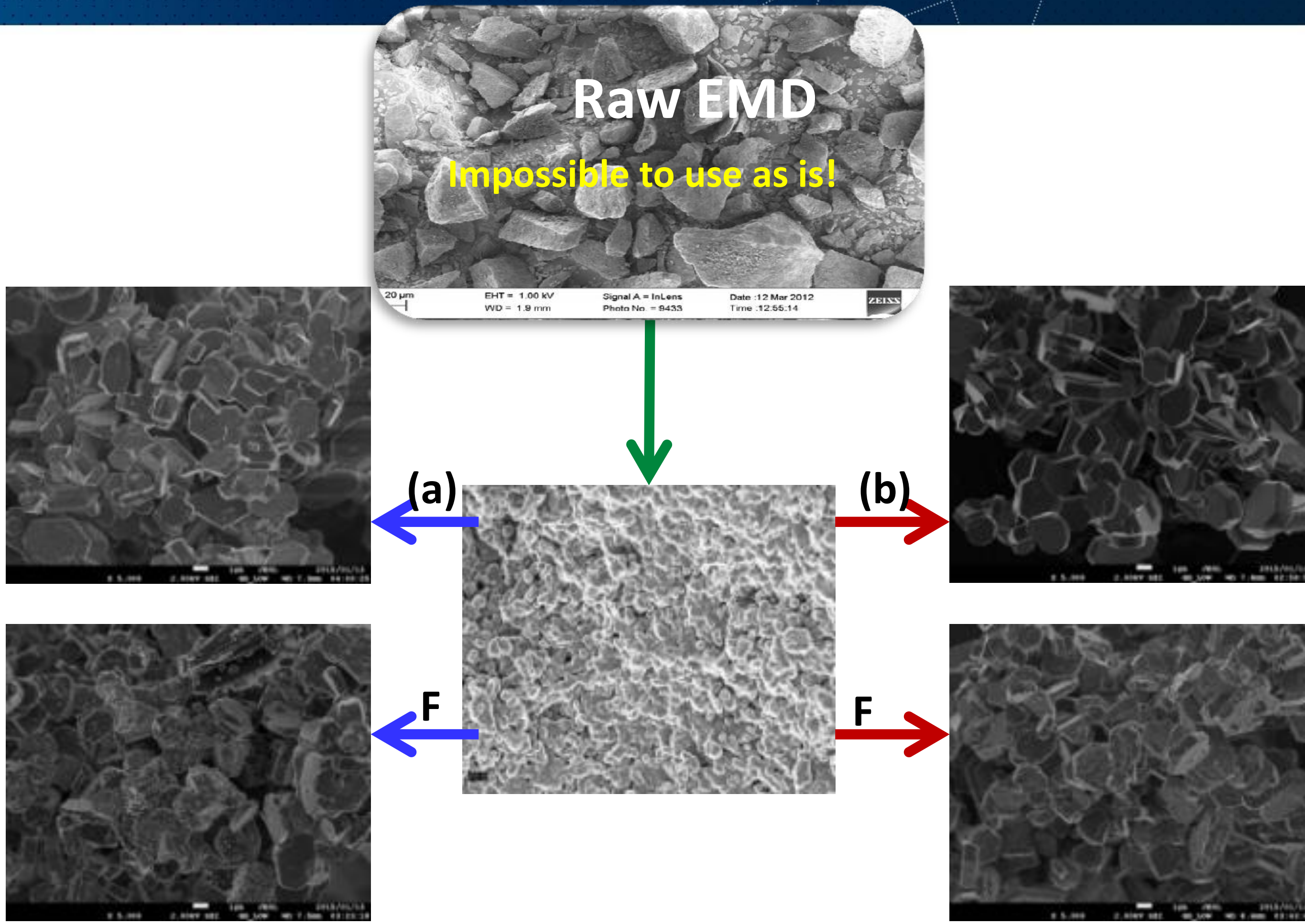


Scalable production of LMO from raw EMD



Note: The materials were crushed during lithiation, a problem???

Scalable production of fluorinated sodium-ion battery cathode materials from raw EMD



CSIR Invention Disclosure /RSA patent application in progress

CSIR Energy Storage RD&I Laboratory

CSIR RD&I Impact Pathway on Energy Storage

Reactor

Cathode materials
(Powder > 1 kg)

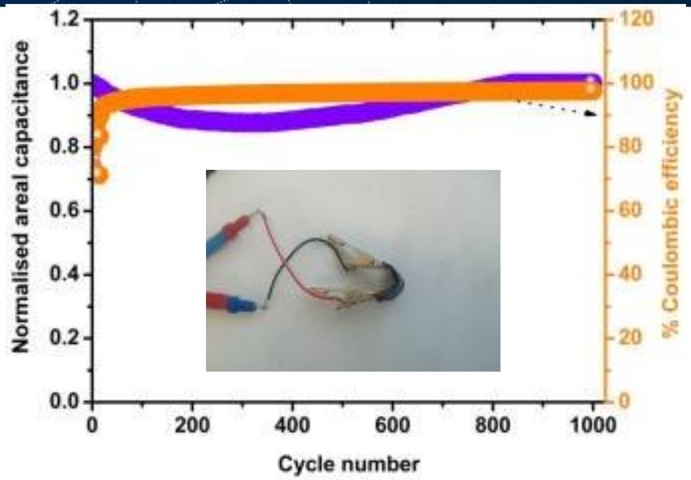
Cells/Packs

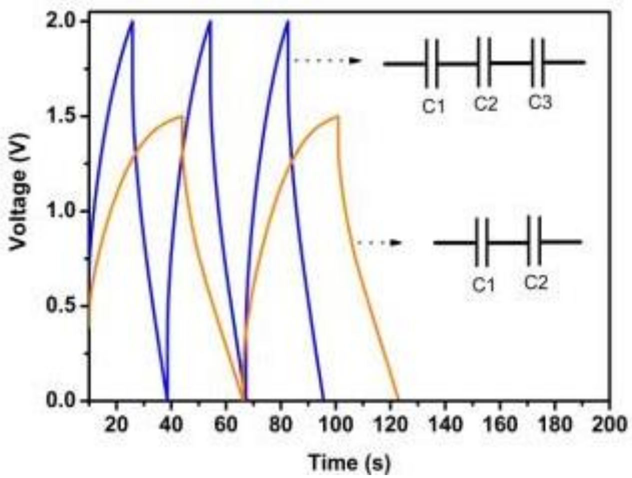
Tech demo

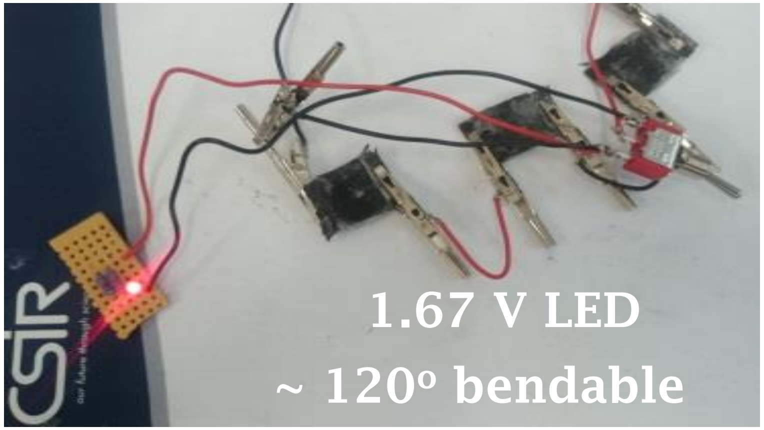
Products: LMO, LMNO, NMC, Mn-based Supercaps

Source: Wikipedia images

Typical all-solid-state flexible supercapacitor







CSIR Invention Disclosure /RSA patent application in progress

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Thank you