Innovative hybrid high voltage electrodes based on LMNO/LFP materials for lithium-ion batteries

Daniele Versaci [(a)], Roberto Colombo [(a)], Giorgio Montinaro [(a)], Mihaela Buga [(b)], Carlotta Francia [(a)], Julia Amici [(a)], Silvia Bodoardo [(a)]

(a) Electrochemistry Group, Department of Applied Science and Technology (DISAT), Politecnico di Torino, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy
(b) National Research and Development Institute for Cryogenic and Isotopic Technologies – ICSI Rm. Valcea, 240002, Romania

NanoInnovation 2024 Conference & Exhibition — Rome, 9-13 September

Introduction

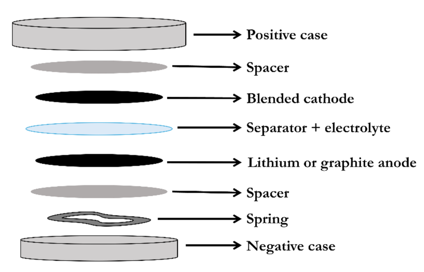
Electrochemical energy-storage systems, such as lithium-ion batteries (LiBs), have turned out to be the most prevalent technology for a wide range of devices. However, to meet the ever-increasing market demand, significant effort is still needed to develop batteries with better performance in terms of power and energy density [1]. In this frame, cathode materials completely cobalt-free and operating at high voltage, such as LNMO (lithium nickel manganese oxide) are particularly interesting and potentially able to increase the electrochemical performance of next-generation high-energy-density LiBs. Unfortunately, LNMO still suffers of some drawbacks such as easy cation leaching during cycling and electrolyte decomposition at high voltage. One possible approach to mitigate these issues, increasing the safety of the system, the lifetime, and limiting the cost, is using blended electrodes, containing multiple types of active materials [2].

In the present work, within HYDRA H2020 project, the influence of LFP (lithium iron phosphate) physically mixed with LMNO was studied both from the morphological and electrochemical point of view. The role of LFP was studied by changing its amount inside the cathode formulation and the electrochemical properties were evaluated both in half-cell and full-cell configurations. In particular, the simple and up-scalable physical blending, by resonant acoustic mixing technique, provided a good distribution of LFP and LNMO particles, resulting in increased electrochemical performances [3].

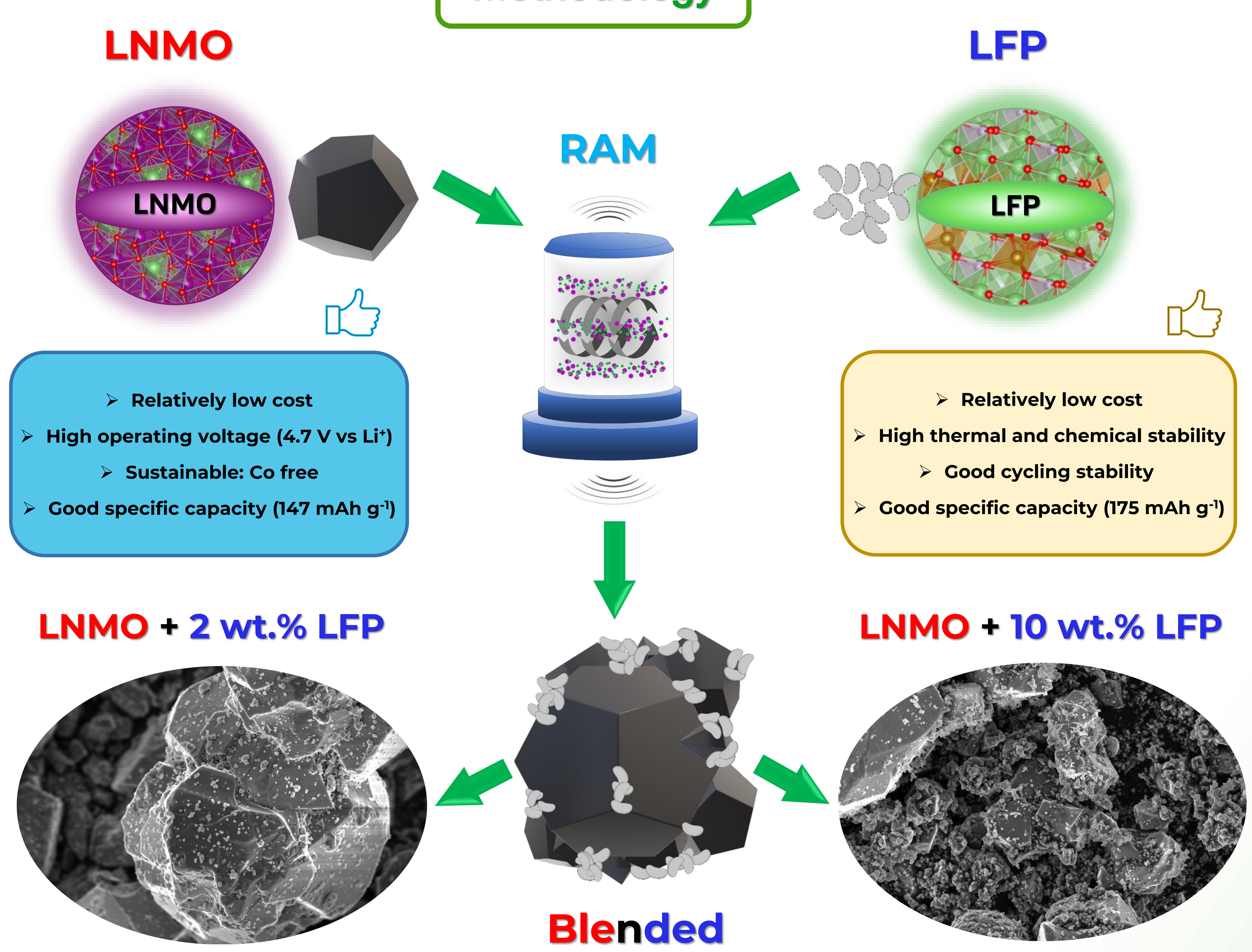
Experimental

Electrode preparation and testing:

- Electrode composition: 95:5:5 wt.% (Active material$_4$:Super C65:binder)
- Slurry deposition: automatic doctor blade casting on carbon-coated aluminum foil
- Electrode mass loading 10.5–11.5 mg cm^{-2}
- Type of cell: half-cell, full-cell, 3-electrodes cell
- Counter/reference electrode: Li metal or graphite
- N/P (full-cell): 1.1
- Electrolyte: Electrolyte : 1.2 M LiPF$_6$ (EC:EMC 3:7) + 5% FEC
- Cycling protocol: charge CC-CV, discharge CC
- Voltage range: 3.0 V – 4.75 V

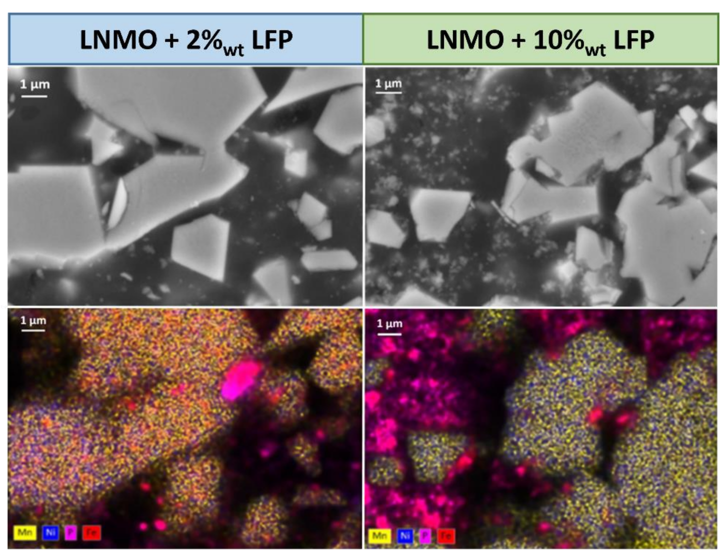


Methodology

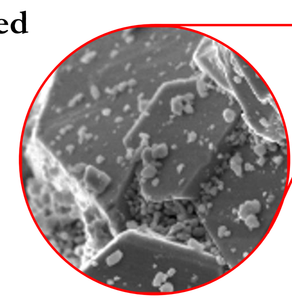


Material characterization

FESEM/EDX → LFP distribution on LNMO particles using RAM



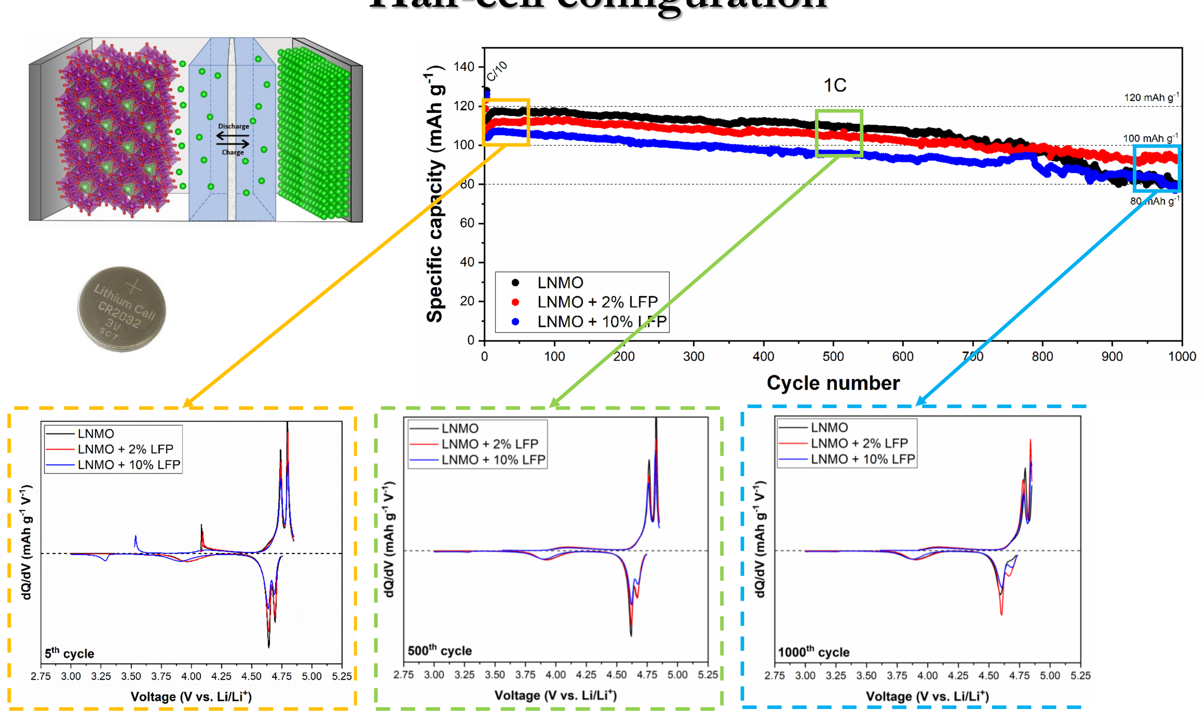
- RAM parameters: 5 min 100G – 5 min pause - % min 100G
- Mixing time is considerably reduced
- No damage of the mixed particles
- Good blending uniformity

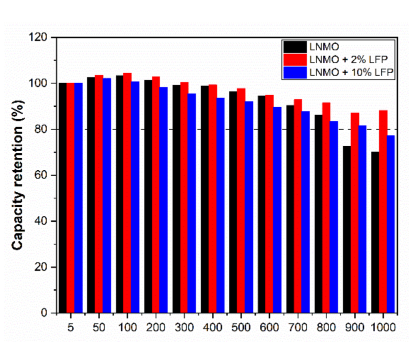


- LFP particles (200 – 300 nm) fill the voids between larger LNMO particles (> 1 μm)
- 2% LFP → better distribution of LFP particles

Electrochemical characterization

Half-cell configuration



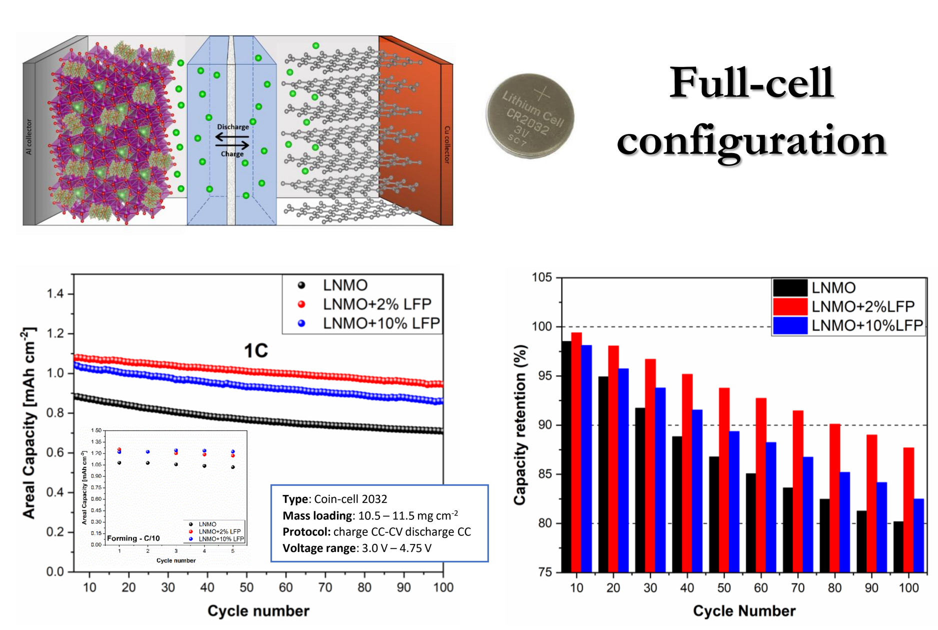


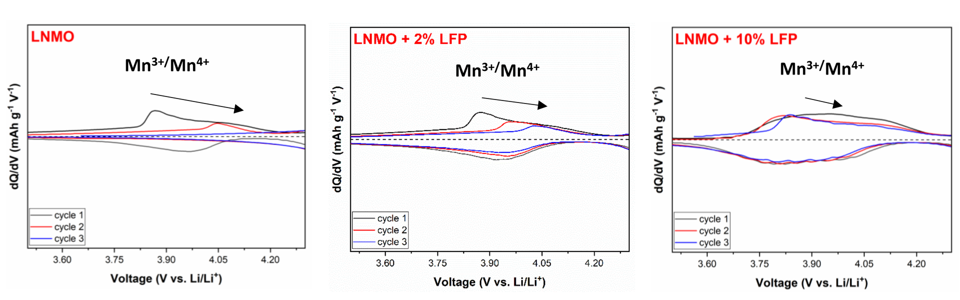
- specific capacity higher for pure LNMO

But…

- initial potential confirms the presence of electrochemical active LFP → effect of LFP is detectable up to 1C
- higher capacity retention (> 80%) for blended cathodes after 800 cycles
- huge polarization for pure LNMO cathode → shift of Ni$^{2+/4+}$ peaks

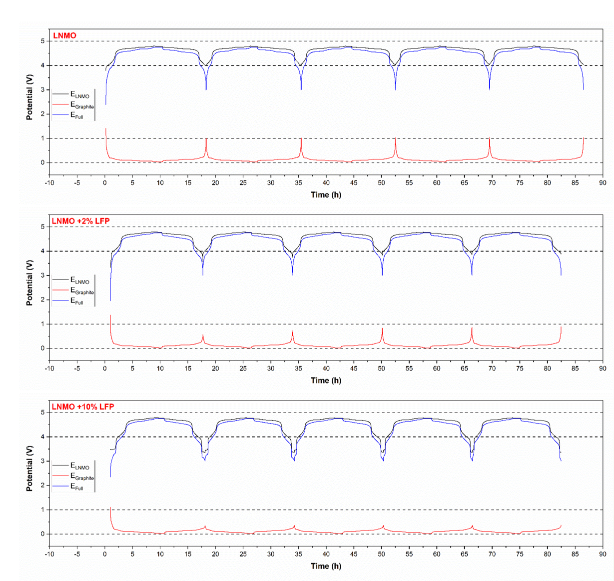
Full-cell configuration

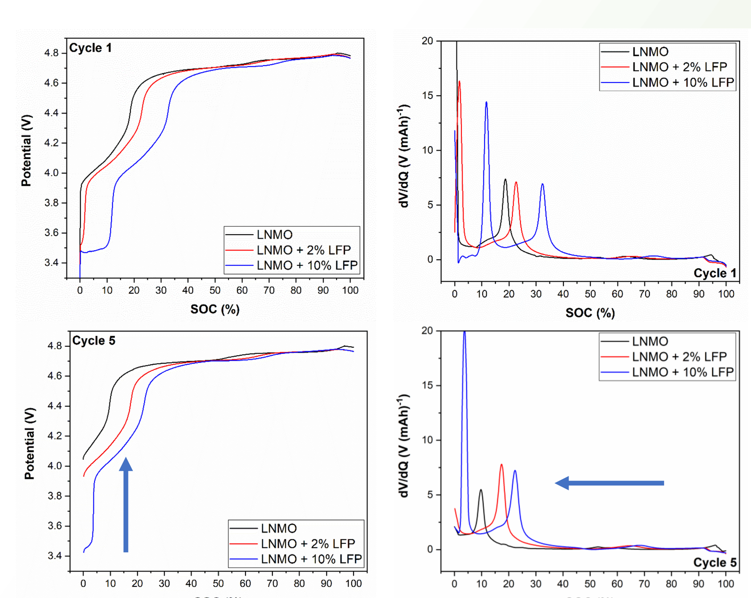


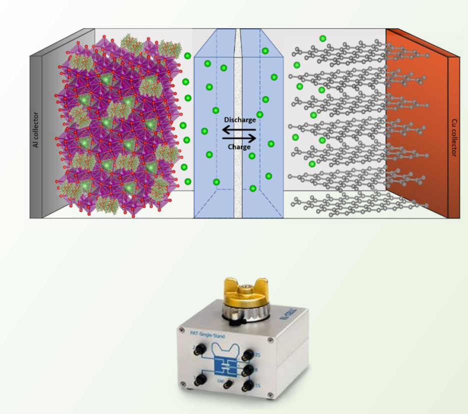


- Higher specific capacity and capacity retention for LNMO + 2%LFP (> 85%)
- shift of Mn $^{3+/4+}$ peaks potential → higher polarization for pure LNMO
- LFP → buffer effect

Three electrodes-cell configuration







- Increasing of LNMO potential → higher polarization → lithium loss
- Lower voltage plateau → skipped due to Li loss
- LFP → reduce the potential drift (of the cathode) → Li⁺ loss compensation

Conclusions

- Resonant acoustic mixing (RAM) is a suitable technique to physically blend LFP and LNMO → good particles distribution
- Lower amount of LFP (2%wt) reduces the formation of particles agglomerates → higher electrode homogeneity
- The electrode reaction is dominated by LFP at low potentials (< 3.9 V) and by LNMO at high potentials (> 3.9 V) at lower C-rates
- The presence of appropriate amount of LFP allows reaching higher full cell electrochemical performances → reducing the polarization of the cells and increasing the capacity retention
- LFP can compensate the LNMO lithium loss during cycling
- Concomitant electrochemical and morphological factors are responsable for the increased performances of blended LNMO/LFP electrode

Do you want to have more info? → **Have a look to our paper!!!**

References:

[1] Amici et al. Adv. Energy Mater. 2022, 12, 2102785
[2] Heubner et al. Batteries & Supercaps 2022, 5, e202100171
[3] Versaci et al. Journal of Power Sources 2024, 613, 234955

Acknowledgments: Authors kindly acknowledge the European Community for funding Hydra Project (GA 875527)
Daniele Versaci wish to thank DM 1062/2021 program for the support