Lithium Rich Transition Metal Oxides as high capacity positive electrode materials in Li-ion cells

Arcangelo Celeste, Vittorio Pellegrini, Sergio Brutti, Laura Silvestri

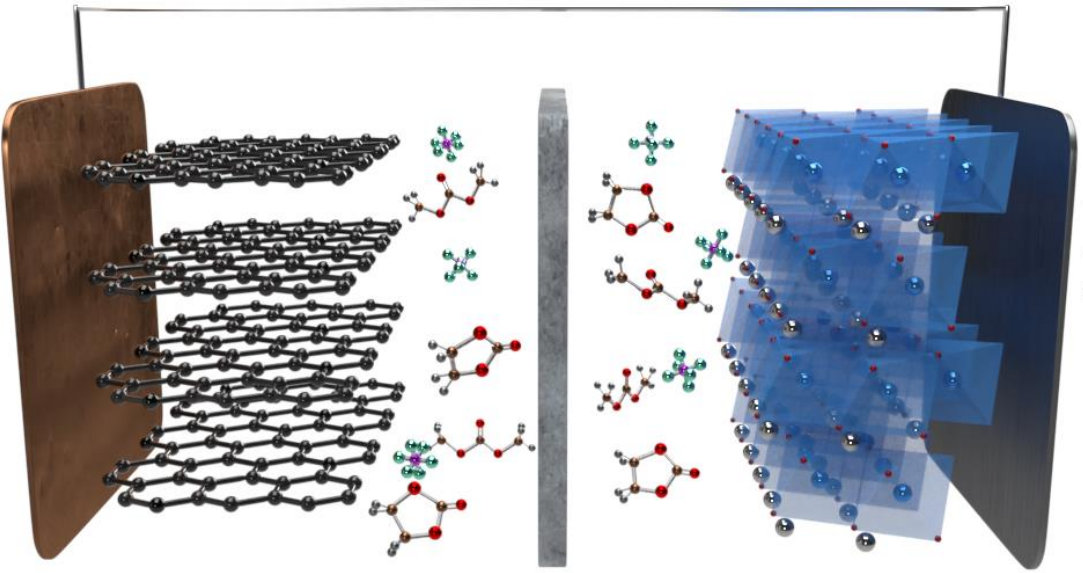
Nanoinnovation, Roma
17th September 2020

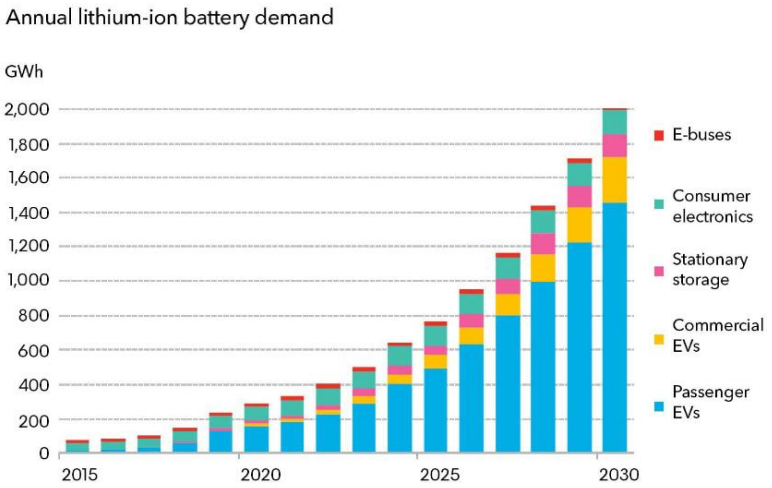
ISTITUTO ITALIANO DI TECNOLOGIA
GRAPHENE LABS

UNIVERSITÀ DEGLI STUDI DI GENOVA

Introduction

Lithium Ion Batteries

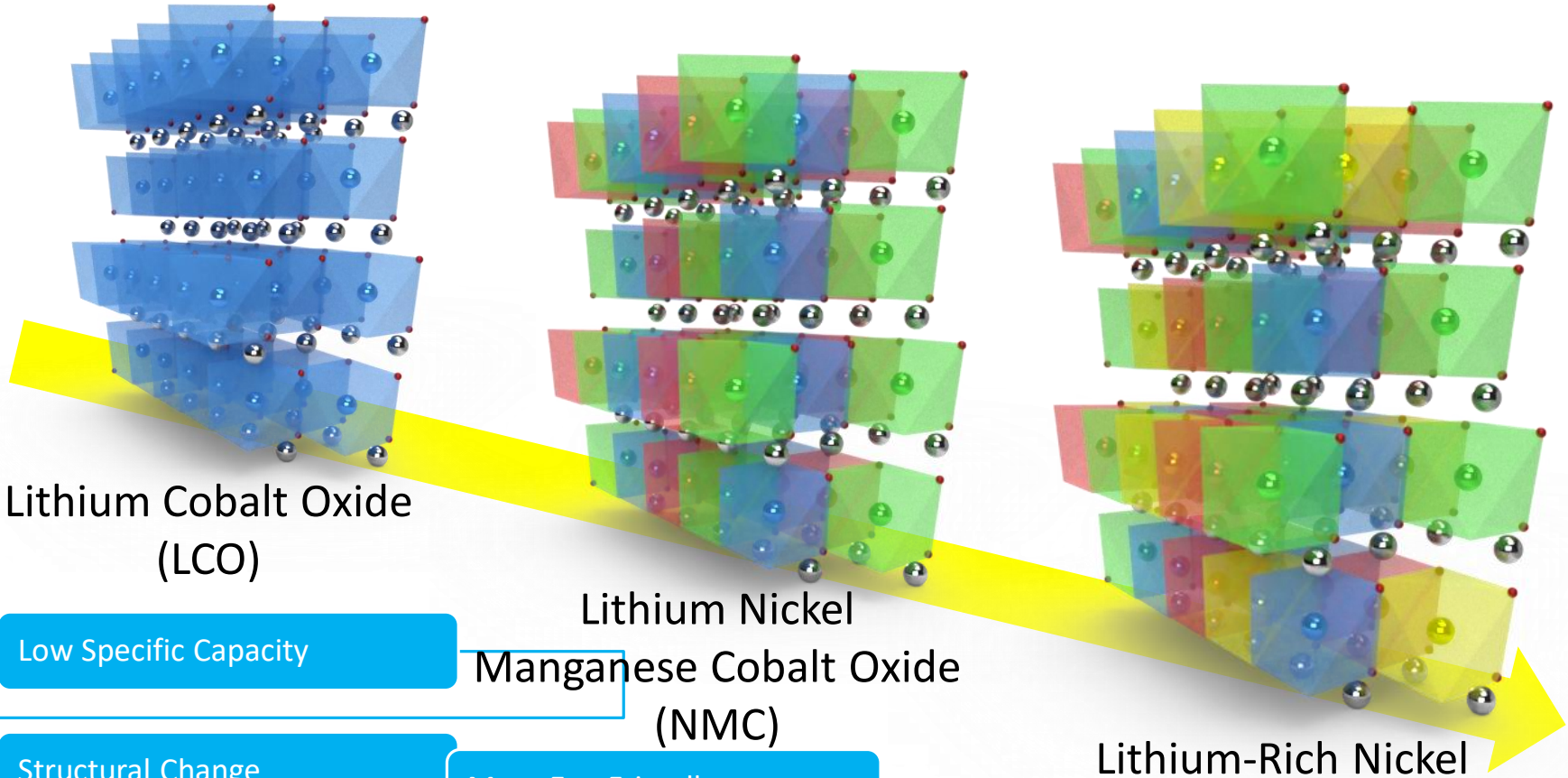




Nanoinnovation, Roma
17th September 2020

Introduction

Li-rich Transition Metals Layered Oxides



Lithium Cobalt Oxide (LCO)

Low Specific Capacity

Structural Change

Cobalt is toxic and expensive

Lithium Nickel Manganese Cobalt Oxide (NMC)

More Eco-Friendly

Poor Rate Capability

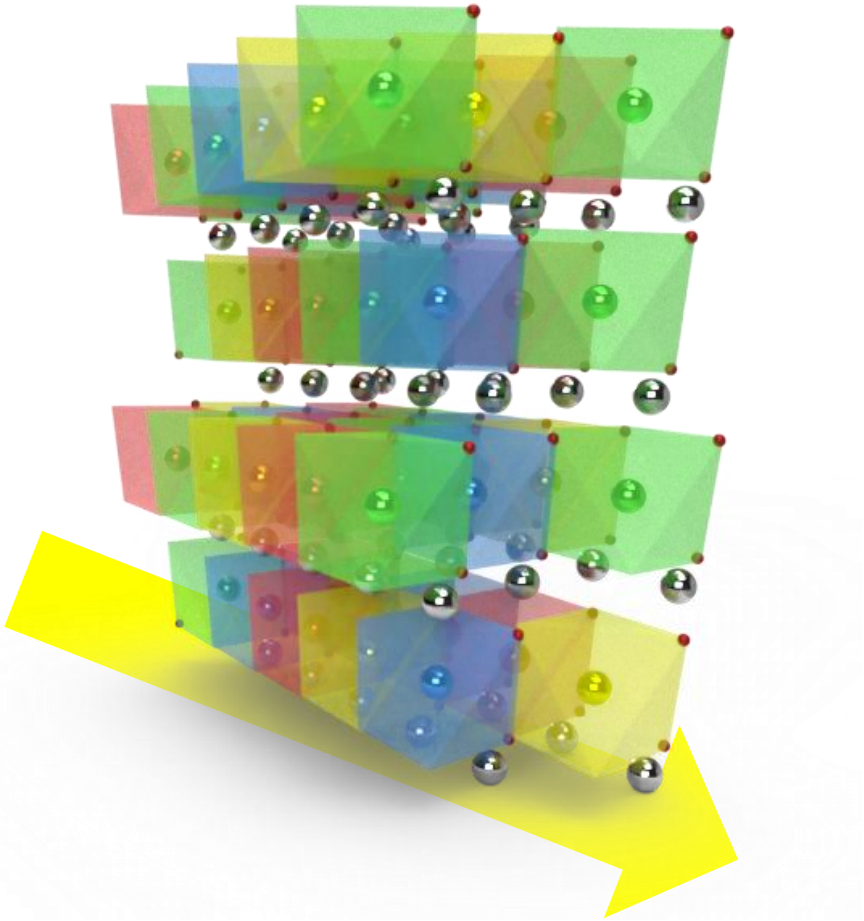
Low Specific Capacity

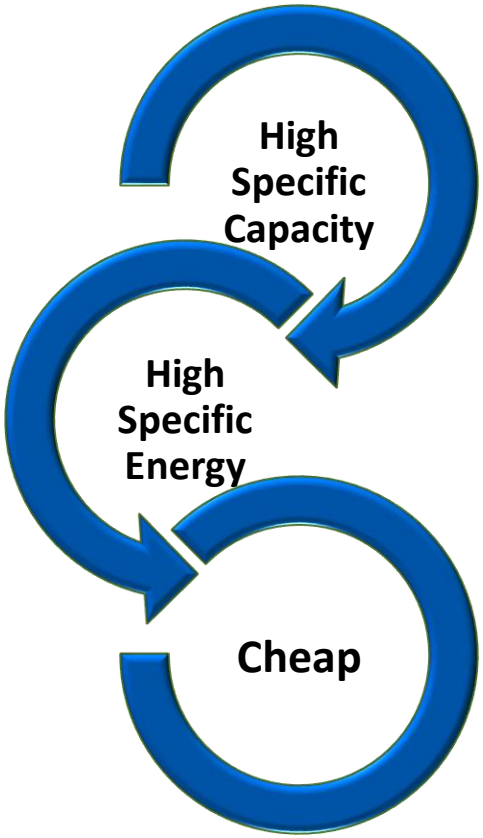
Lithium-Rich Nickel Manganese Cobalt Oxide (LR-NMC)

Lithium
Cobalt
Nickel
Manganese

Introduction

Li-rich Transition Metals Layered Oxides



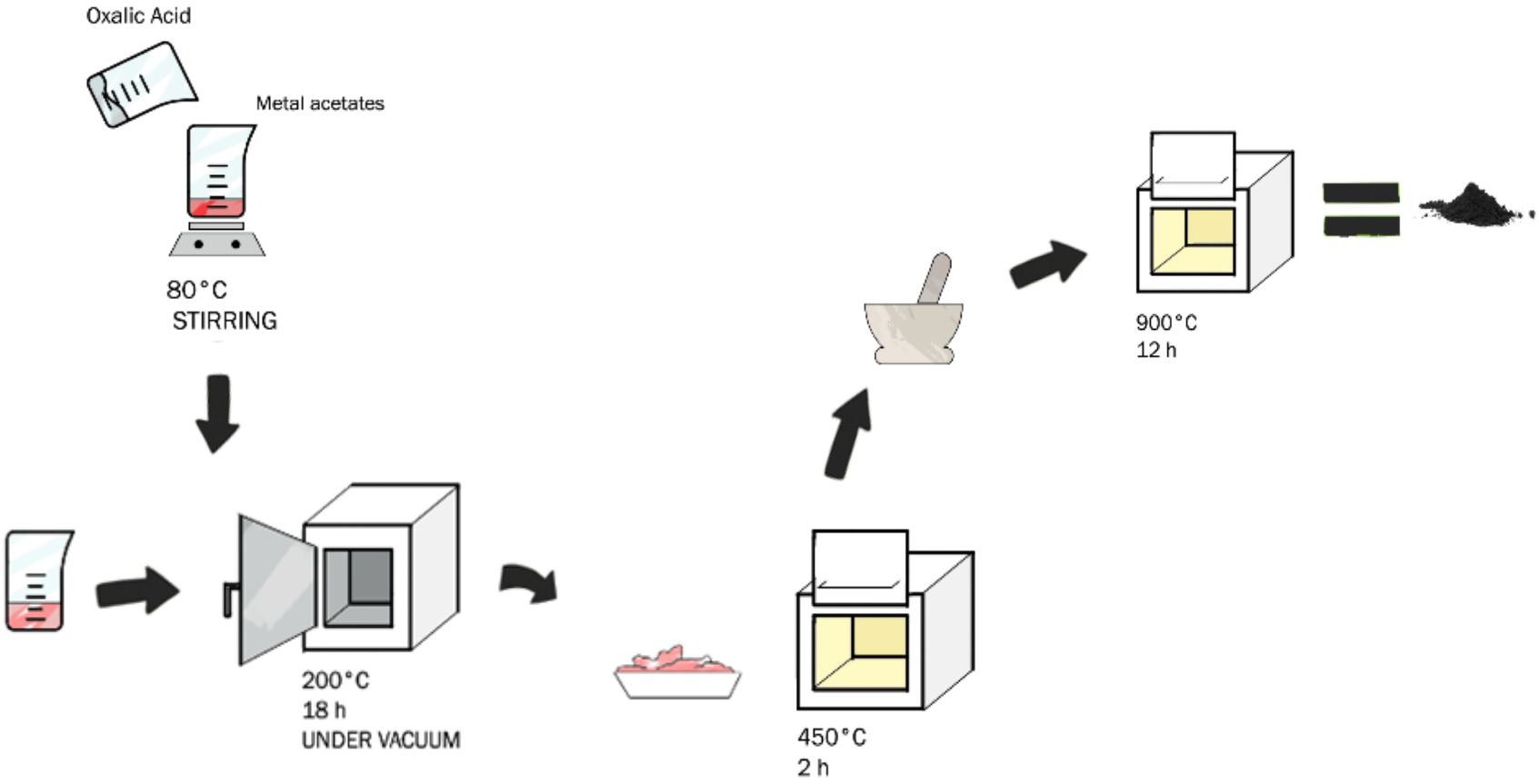


$$Li_{1+x}[NiCoMn]_{1-x}O_2 \leftrightarrows zLi^+ + ze^- + Li_{(1+x-z)}[NiCoMn]_{1-x}O_2$$

Outline

- Synthesis of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$
- X-Ray Diffracion and Rietveld
- Scanning Electron Microscope, Energy-Dispersive X-Ray Spectroscopy
- Galvanostatic Cycling
- Cyclic Voltammentry
- Li-ion Battery test

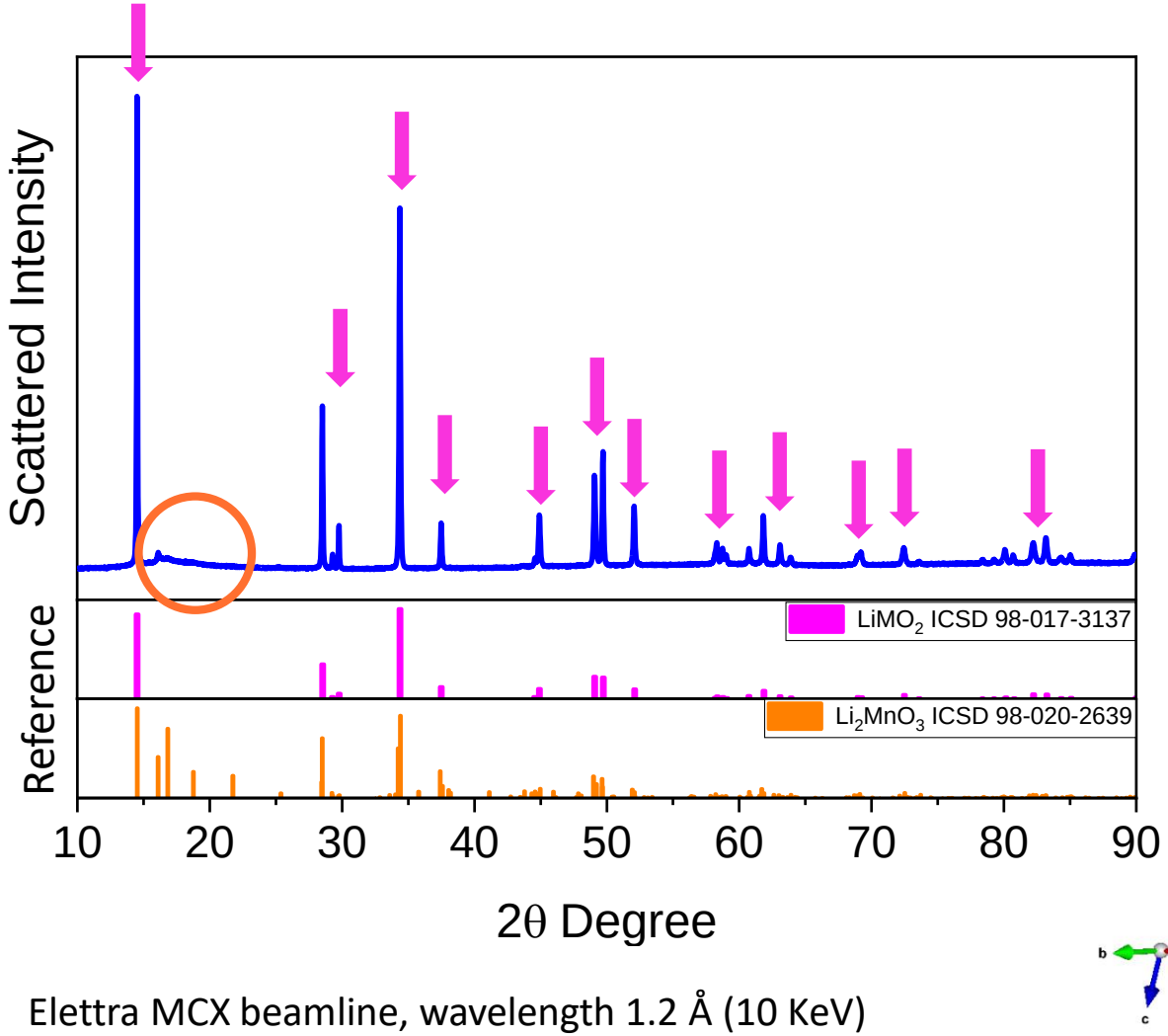
Sol-Gel Synthesis of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$

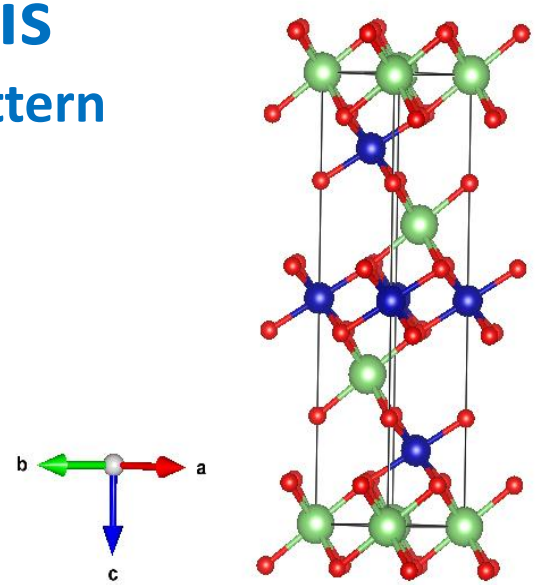


- Stoichiometric Ratio **$C_2H_2O_4$: M = 1.5:1**
- pH value was controlled with **ammonia**

Structural Analysis

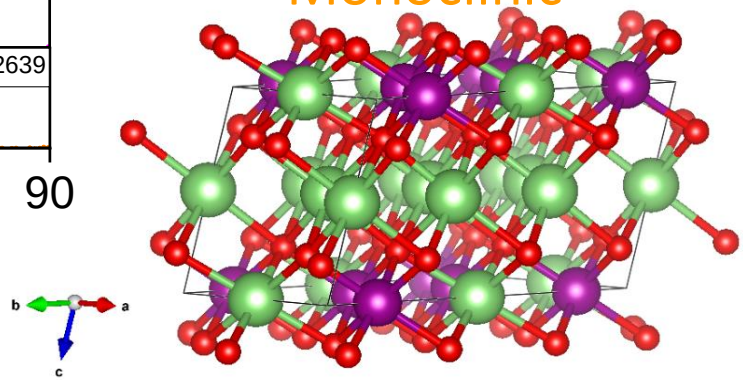
Synchrotron Diffraction Pattern





Rhombohedral

Monoclinic



Elettra MCX beamline, wavelength 1.2 Å (10 KeV)

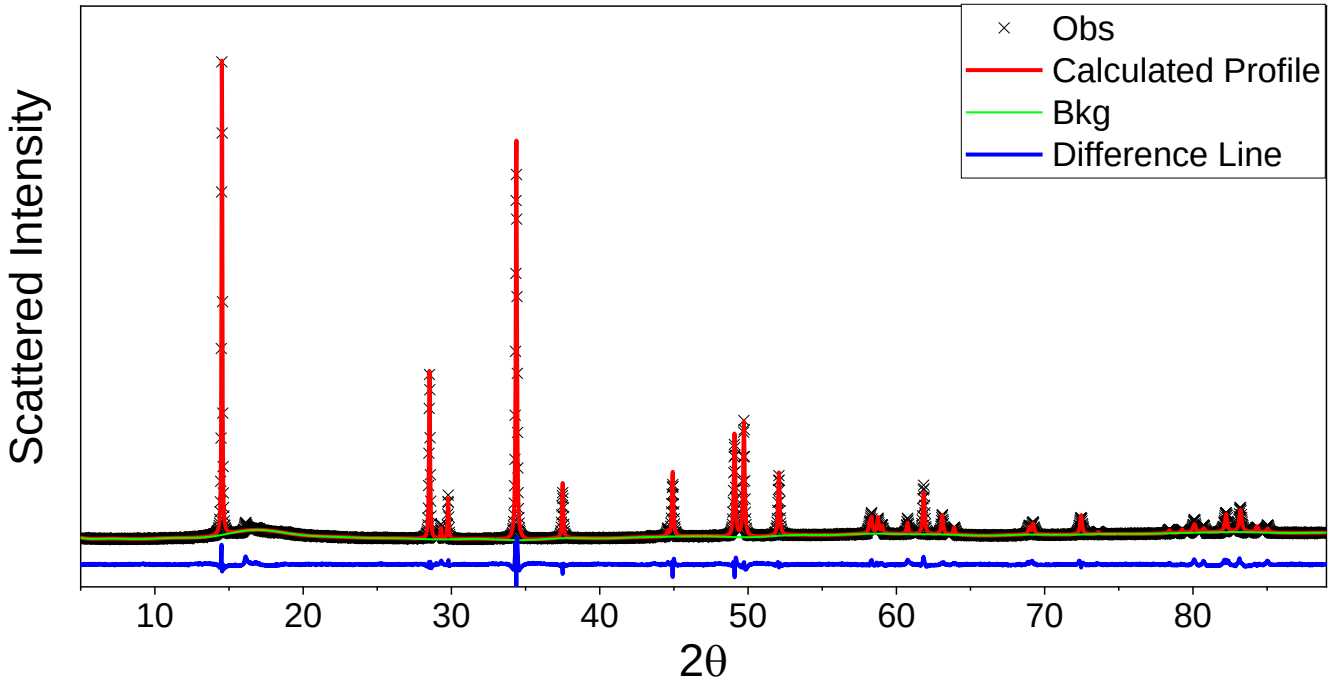
$10° \leq 2\theta \leq 90°$

Nanoinnovation, Roma

17th September 2020

Structural Analysis

Rietveld Refinement



Stoichiometry				wR(%)	
$Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$				4.55	
Structural Model	**Cell Parameters**	**Atoms**	**Wyckoff Position**	**Atomic Coordinates**	**Occupancies**
R-3m	$a = 2.854$ $b = 14.239$	Li/Ni Mn/Co/Ni/Li O	3b 3a 6c	0, 0, 0.5 0, 0, 0 0, 0, 0.739	0.99/0.01 0.54/0.13/0.12/0.21 1.0

Elettra MCX beamline, wavelength 1.2 Å (10 KeV)

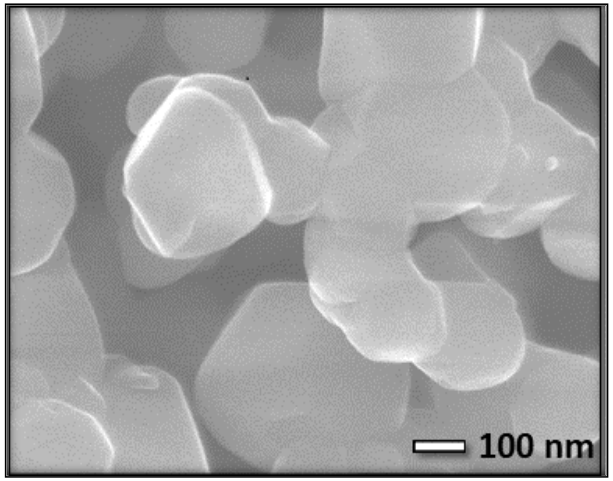
$5° \leq 2\theta \leq 90°$

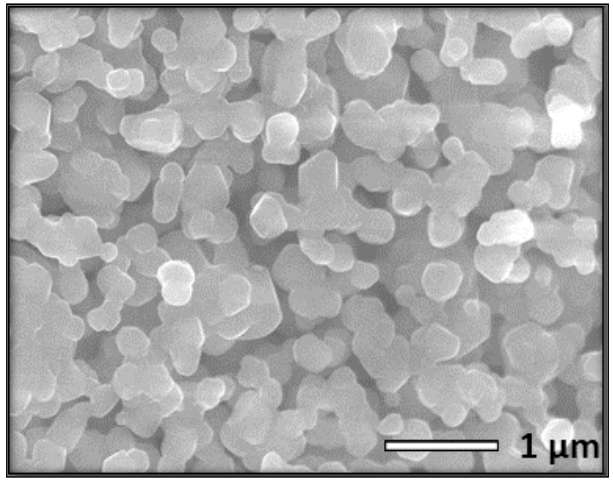
Nanoinnovation, Roma

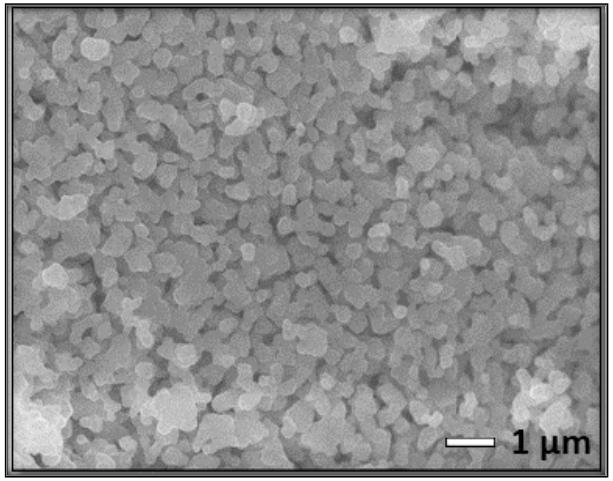
17th September 2020

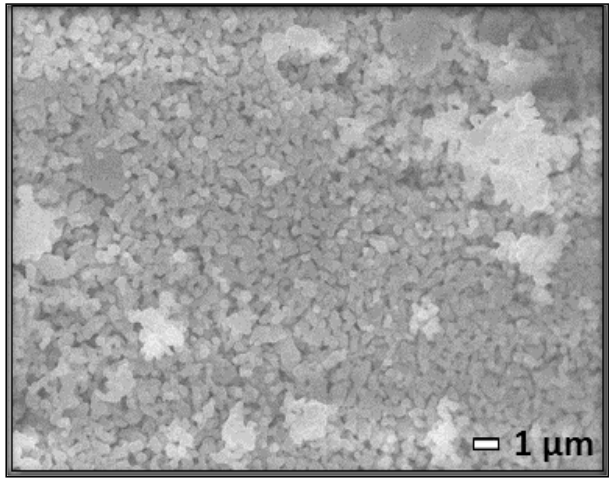
Morphological Analysis

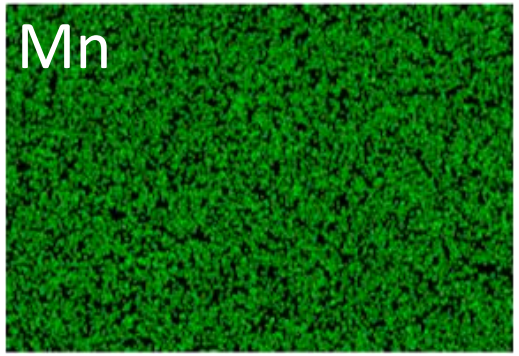
Scanning Electron Microscope – Energy-dispersive X-ray spectroscopy

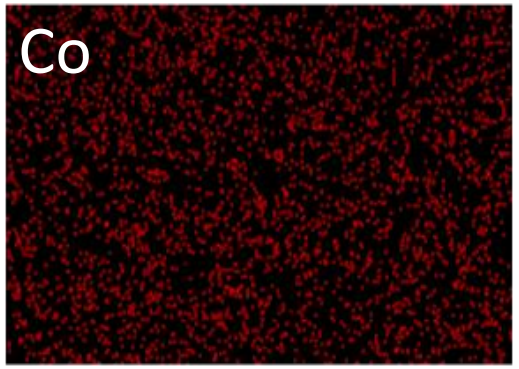


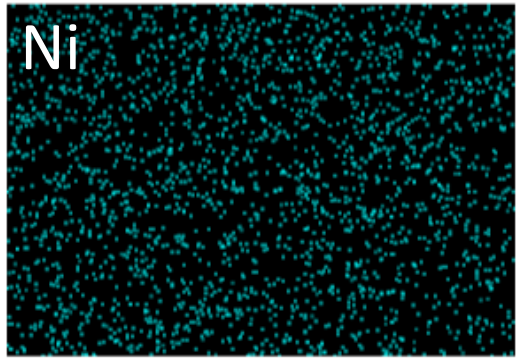








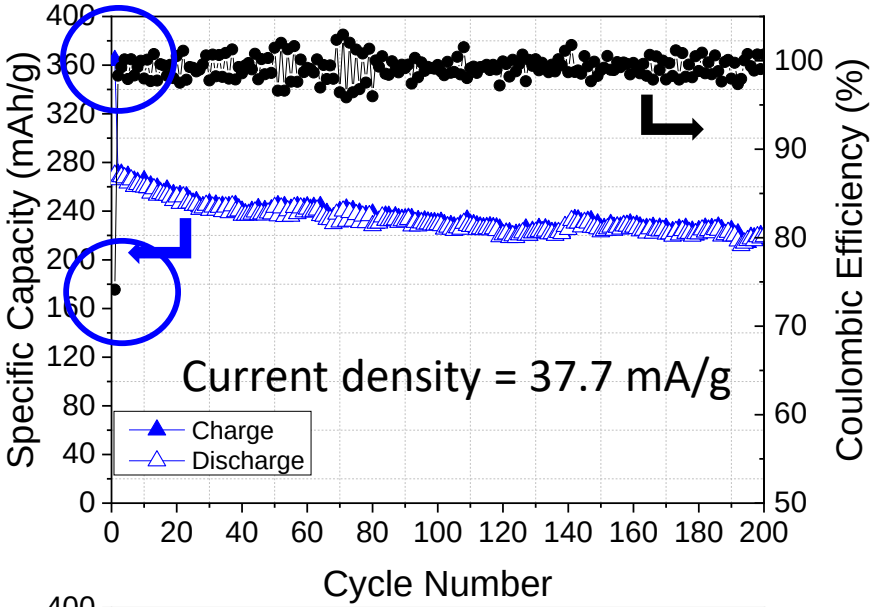


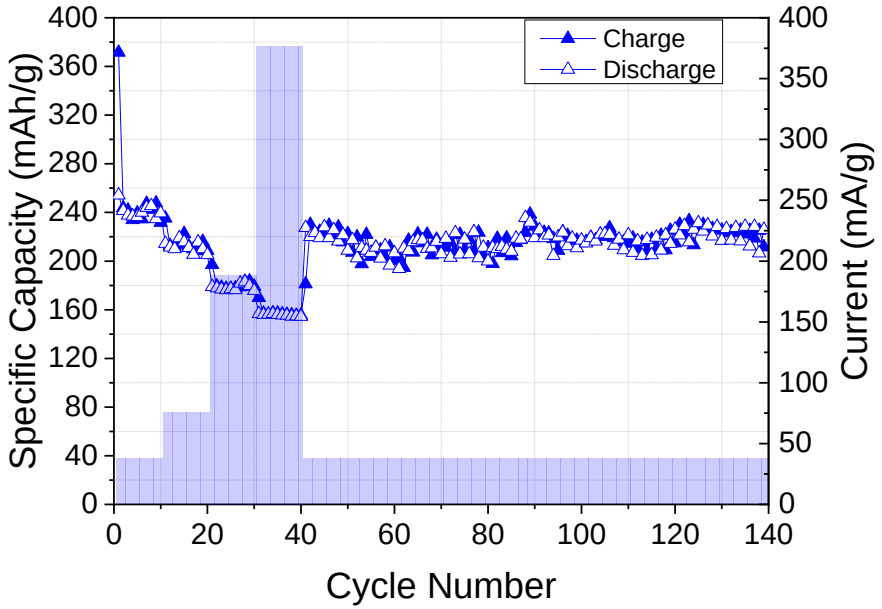


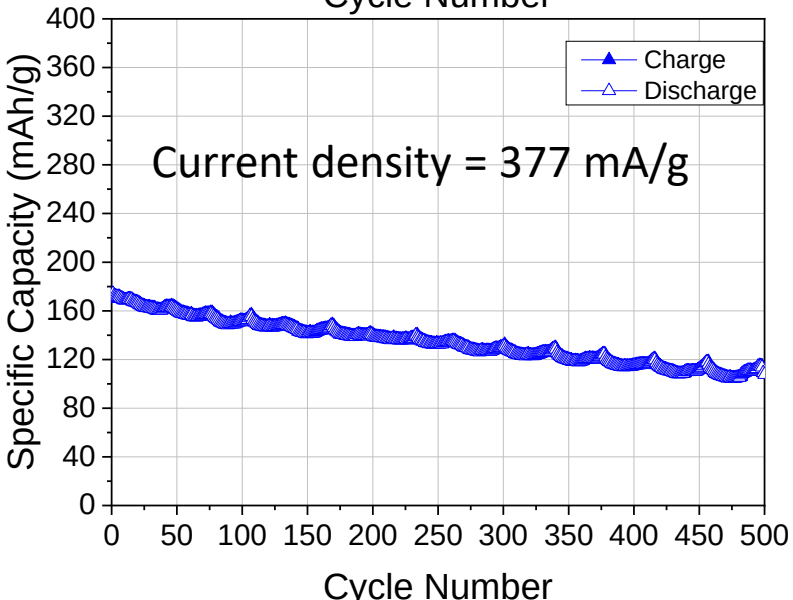
Electrochemical Performances

Galvanostatic Cycling

Li/LP30 (1M $LiPF_6$ in EC:DMC)/LR-NMC 2-4.8V





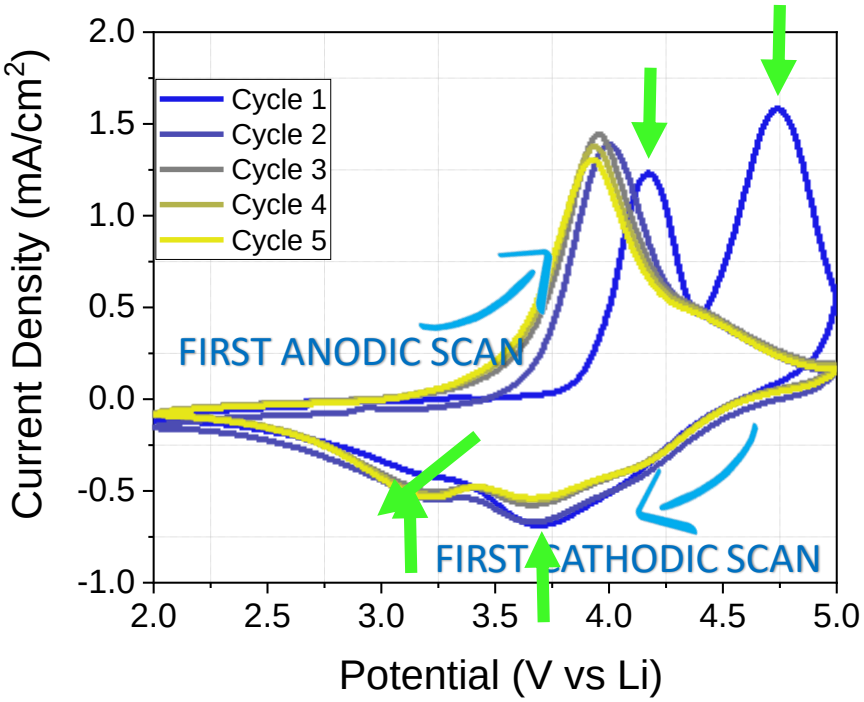


- Specific Capacity over 220 mAh/g.
- LR-NMC is able to substain high currents.
- Capacity Retention is 62% after 500 cycles.

Nanoinnovation, Roma
17th September 2020

Electrochemical Behavior

Cyclic Voltammetry



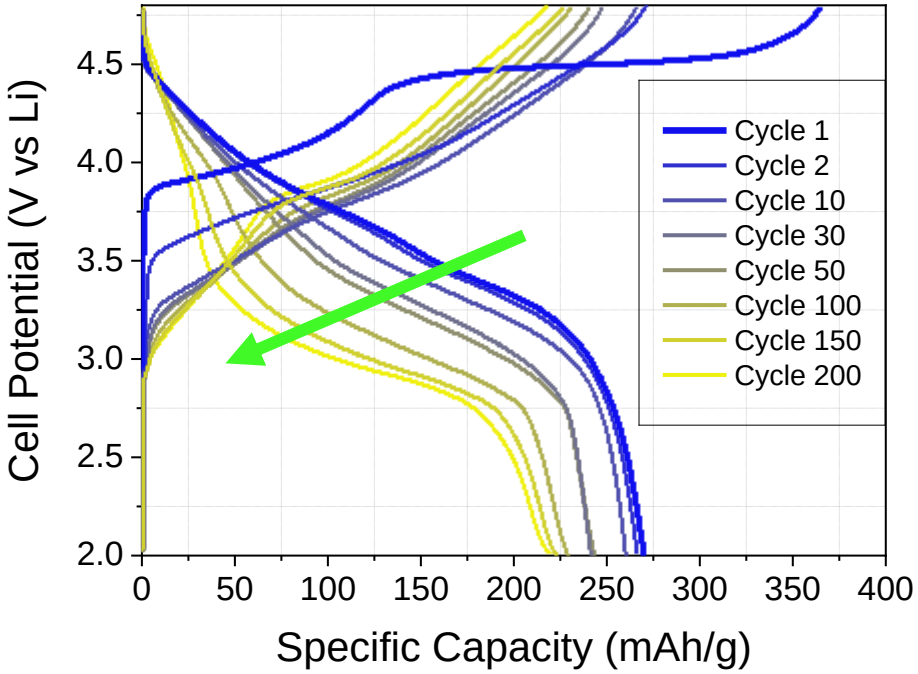
Li/LP30 (1M $LiPF_6$ in EC:DMC)/LR-NMC
2-5 V
Scan rate: 0.5 mV/s

$$Li[M]O_2 \leftrightarrow zLi^+ + ze^- + Li_{(1-z)}[M]O_2$$

$$Li_2MnO_3 \leftrightarrow zLi^+ + ze^- + Li_{(2-z)}MnO_2 + [O^{2-}]$$

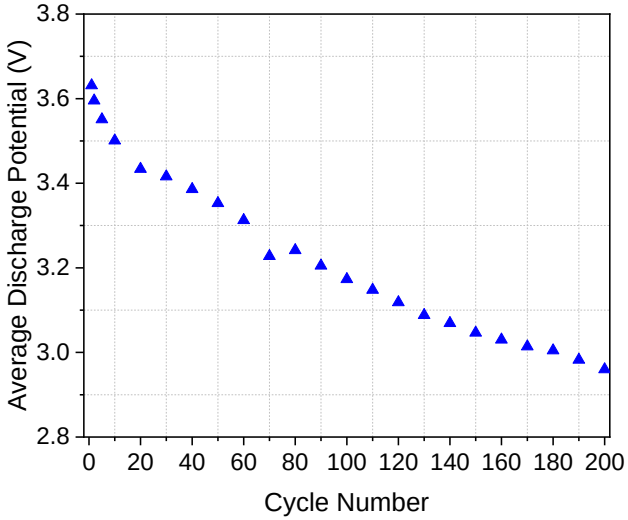
Electrochemical Behavior

Galvanostatic Cycling

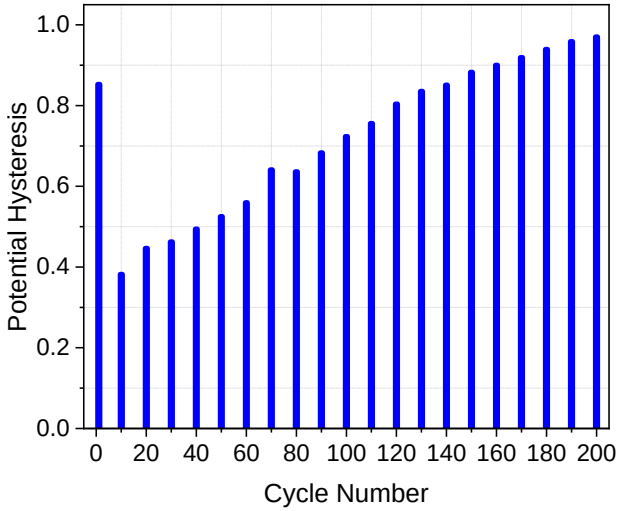


Li/LP30 (1M $LiPF_6$ in EC:DMC)/LR-NMC
2-4.8 V
Current Density: 37.7 mAh/g

VOLTAGE DECAY



INCREASE IN POTENTIAL HYSTERESIS



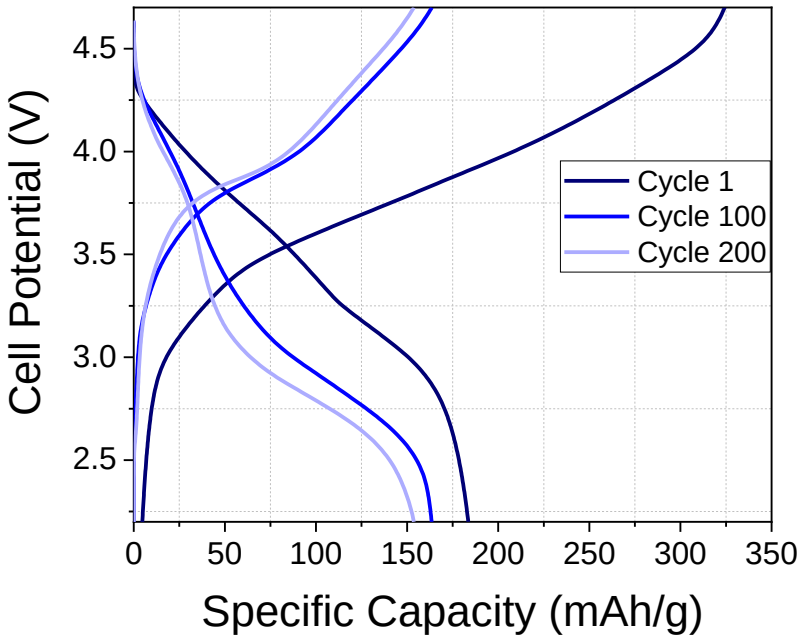
Nanoinnovation, Roma
17th September 2020

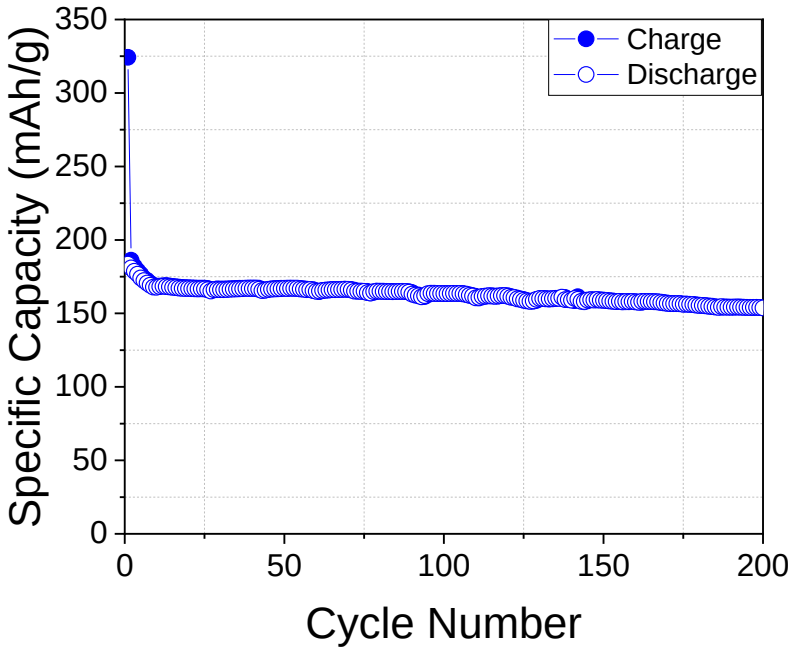
Performances in Li-ion battery

Galvanostatic Cycling

LR-NMC/LP30/Graphite (Pi-Kem)

- Potential range: 2.2-4.7V.
- C-rate: 1C (230 mA/g)





Conclusions

- A simple Sol-Gel synthesis is used to synthetize $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$
- XRD and Rietveld showed a complex structure.
- $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ has a very high electrochemical perfomances.
- Several drawbacks, such as voltage decay and hysteresis increase.

Thank you for your attention!

Nanoinnovation, Roma
17th September 2020