Exploration of $NaMF_3$-M: Mn and Ni perovskites as anodes of lithium-ion batteries.

Liliana T. López Ch., Franklin Jaramillo, Jorge A. Calderón.

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III Escuela Andino-Amazónica de Química
WORKSHOP QUÍMICA Y BIOLOGÍA DE HONGOS CON POTENCIAL BIOTECNOLÓGICO

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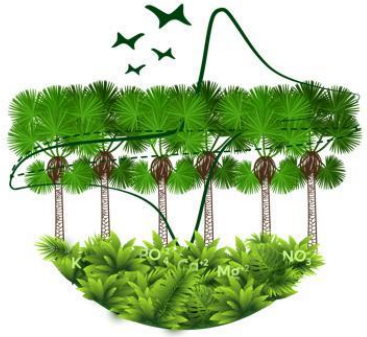

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Outline

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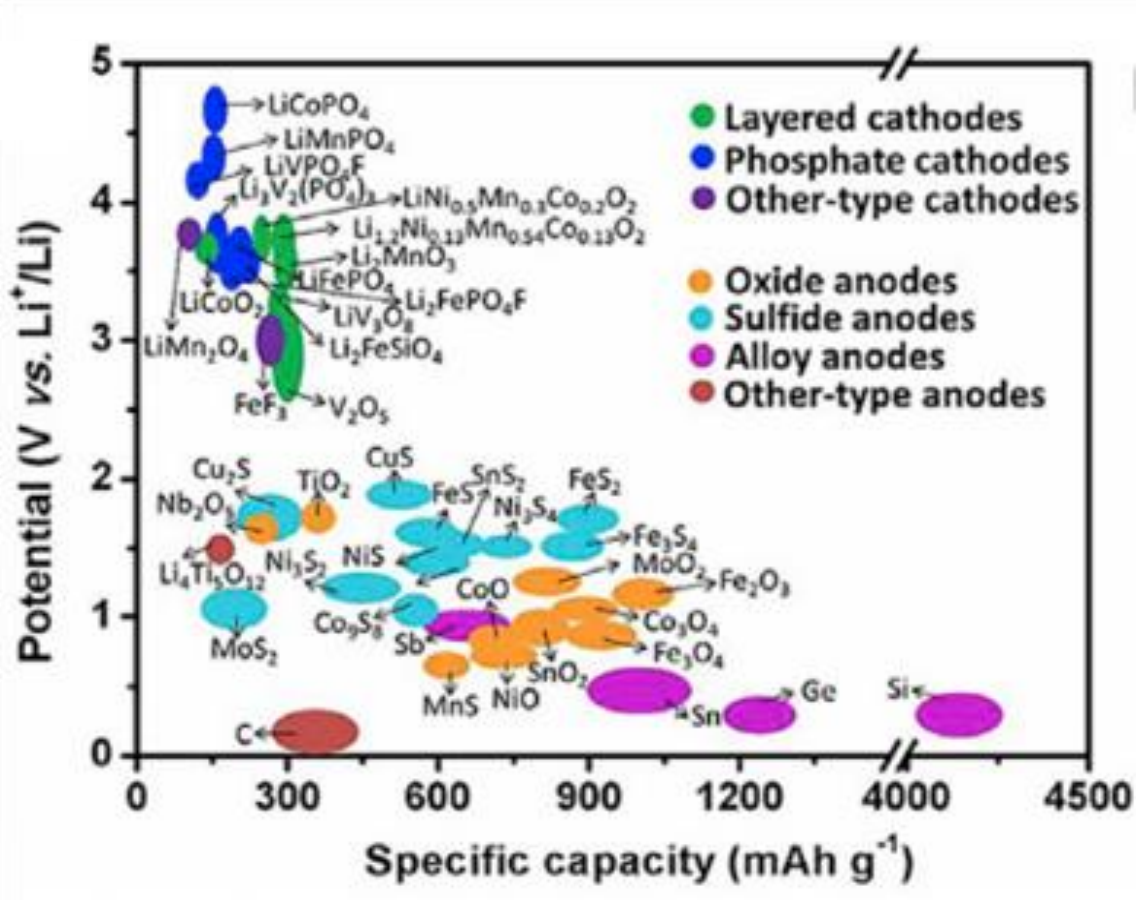
Introduction

Lithium-Ion Battery



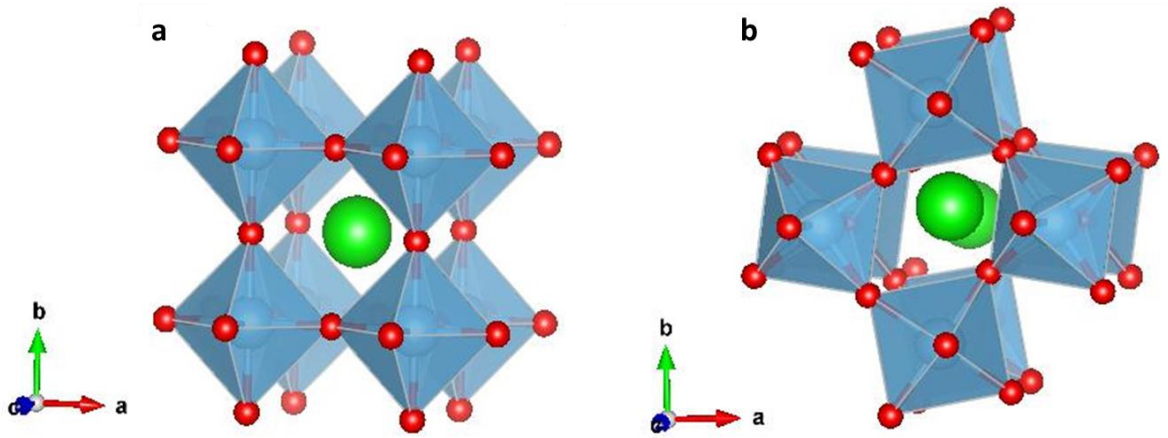
Graphite
- High Capacity
- Abundant content

However

- Short circuit during fast charging-dendrite formation
- Increase electrode potential to avoid lithium deposition

Meng, Jiashen, et al. Joule, 2017, Vol. 1, 522. Lopez L., et. Al., 2020, Electrochimica acta, Vol. 357, 522.

Perovskite materials of metal-halide ABX_3



- A is a metal or organic cation (blue)
- B is a transition metal (green) with 2+ oxidation state.
- X is a halide (red)

Promising candidate as anode of metal-ion batteries

- High ionic mobility
- High theoretical capacity (>200 mAh/g)
- Good structural and thermal stability
- Easy route of synthesis
- Feasible element substitutions

Xu, Qichen, et al., Journal of Physical Chemistry Letters, 2018, Vol. 9, Pag. 6948.

Uribe, José Ignacio, et al., Journal of Physical Chemistry C,, 2016, Vol. 120, Pag. 16393 .

Ramirez, Daniel, et al., Inorganic Chemistry, 2018, Vol. 57, Pag. 4181.

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Perovskites

$NaNiF_3$

Electrochemical tests vs Na showed capacities up to **50** $mAhg^{-1}$ as cathode

Synthesized previously :

- Ball milling
- Solvothermal process
- Electrochemical

Corrosion to obtain NNF/Ni

- Precipitation

$NaMnF_3$

Electrochemical tests vs Na showed capacities of to **165** , **128** and, **50** $mAhg^{-1}$ as cathode

While Theoretical capacity of 190 $mAhg^{-1}$ per atom of Li

$NaMF_3 \not\rightarrow MF_3$

I. D. Gocheva, et al., *J. Power Sources*, 2009, Vol **187**, Pag. 247–252.

N. Dimov, et al., *Electrochim. Acta*, 2013, Vol **110**, Pag. 214–220.

Kitajou A., et al., *Electrochim. Acta*, 2017, Vol **245**, Pag. 424-429.

Nava-Avendaño J. , et al., Solid State Ionics, 2015, Vol **278**, Pag. 106-113,

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Objective

To Obtain $NaMF_3$- M:Ni and Mn

As anode vs Li/Li+

Conversion reaction

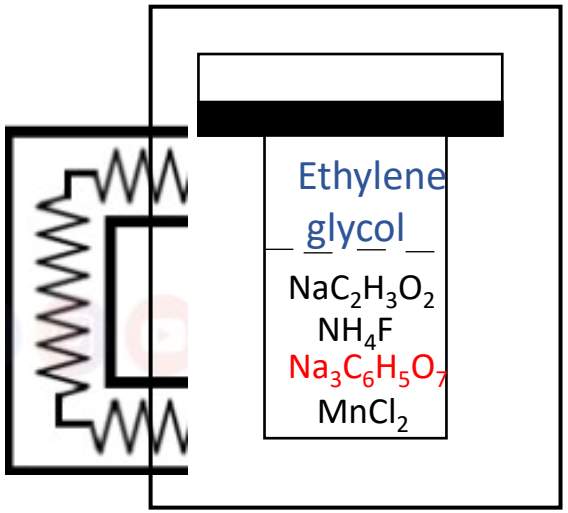
$$NaMF_3 + 2\,Li \longrightarrow M + NaF + 2LiF$$

Theoretical capacities of at least 320 $mAhg^{-1}$ per structure

Methodology

Sample preparation of composite $NaMnF_3$ and $NaNiF_3$

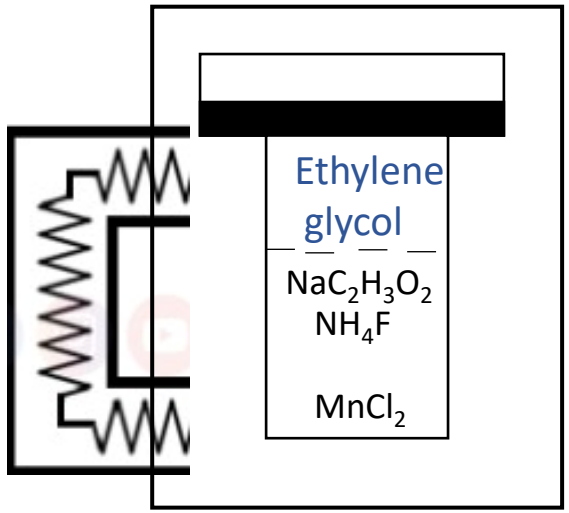
Sample 1



Annealing to 185°C at HT during 24 h

$NaMnF_3$ -NMF_C_HT_24h

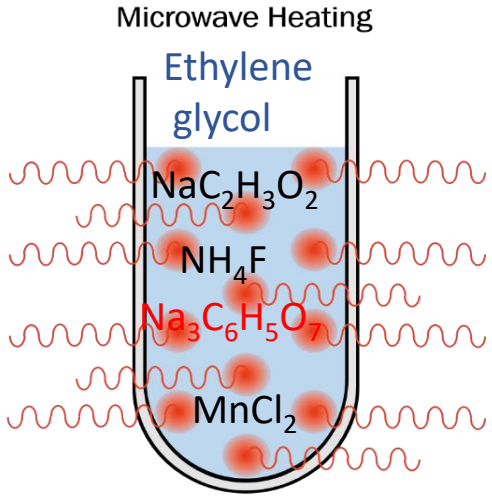
Sample 2



Annealing to 185°C at HT during 24 h

NMF__HT_24h

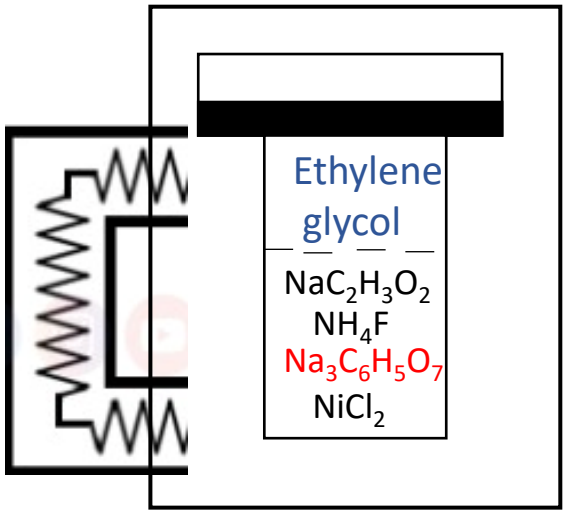
Sample 3



Annealing to 200°C at Microwave during 1 h

NMF_C_Mw_1h

Sample 4



Annealing to 185°C at HT during 24 h

$NaNiF_3$ -NNF_C_HT_24h

Methodology

Sample preparation

Sample 1 **NMF_C_HT_24h**

Sample 2 **NMF__HT_24h**

Sample 3 **NMF_C_Mw_1h**

Sample 4 **NNF_C_HT_24h**

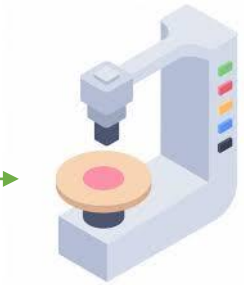
Electrode obtention

- Copper collector
- Active material 70%
- PVDF 10%
- Carbon super P 20%
- Solvent: N-methyl-pyrolidone

Cell assembly

- Glove box
- Argon atmosphere
- Li ref. and counter electrode.

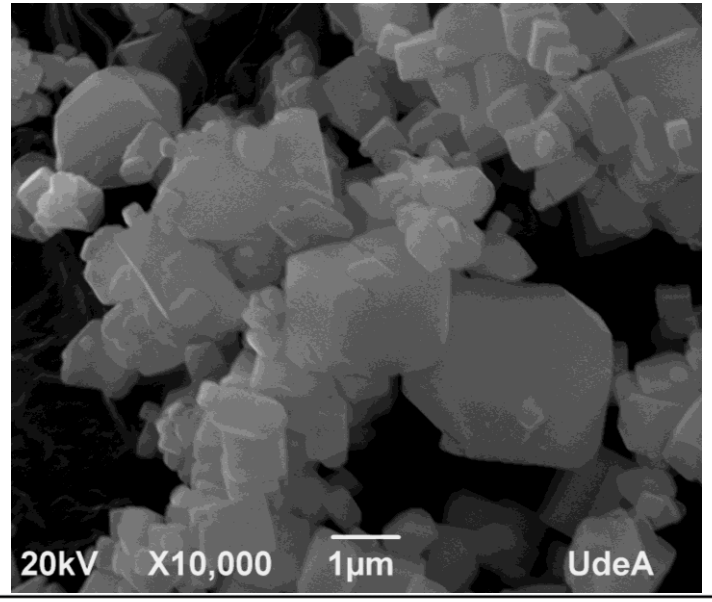
Characterization



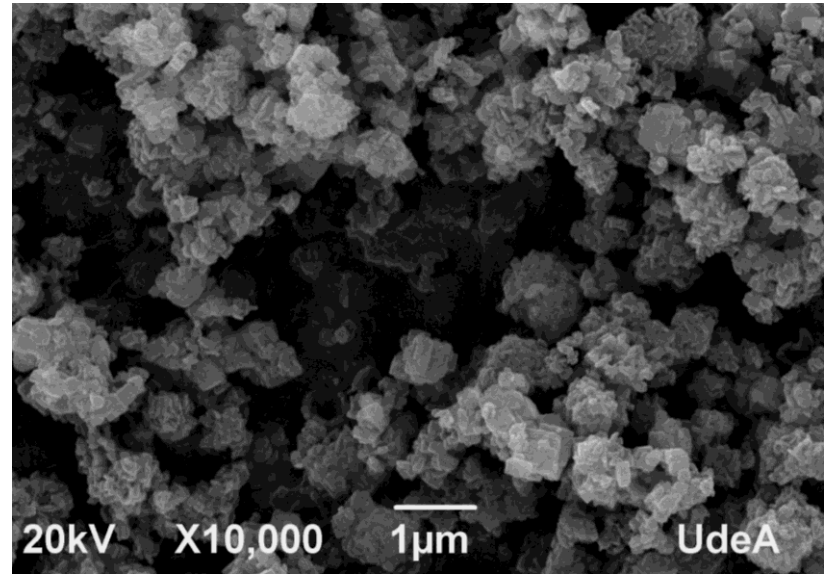
- Electrochemical analysis
- SEM
- TEM

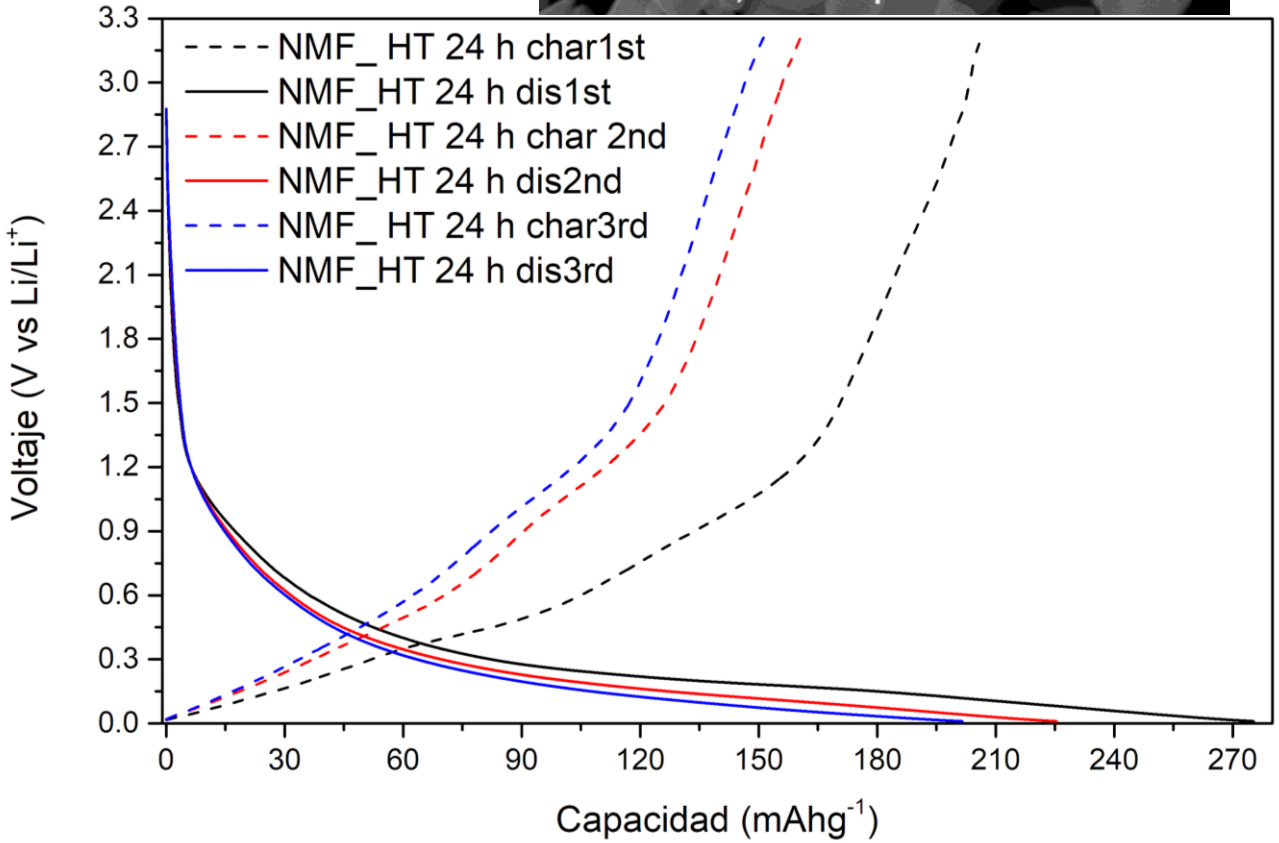
RESULTS

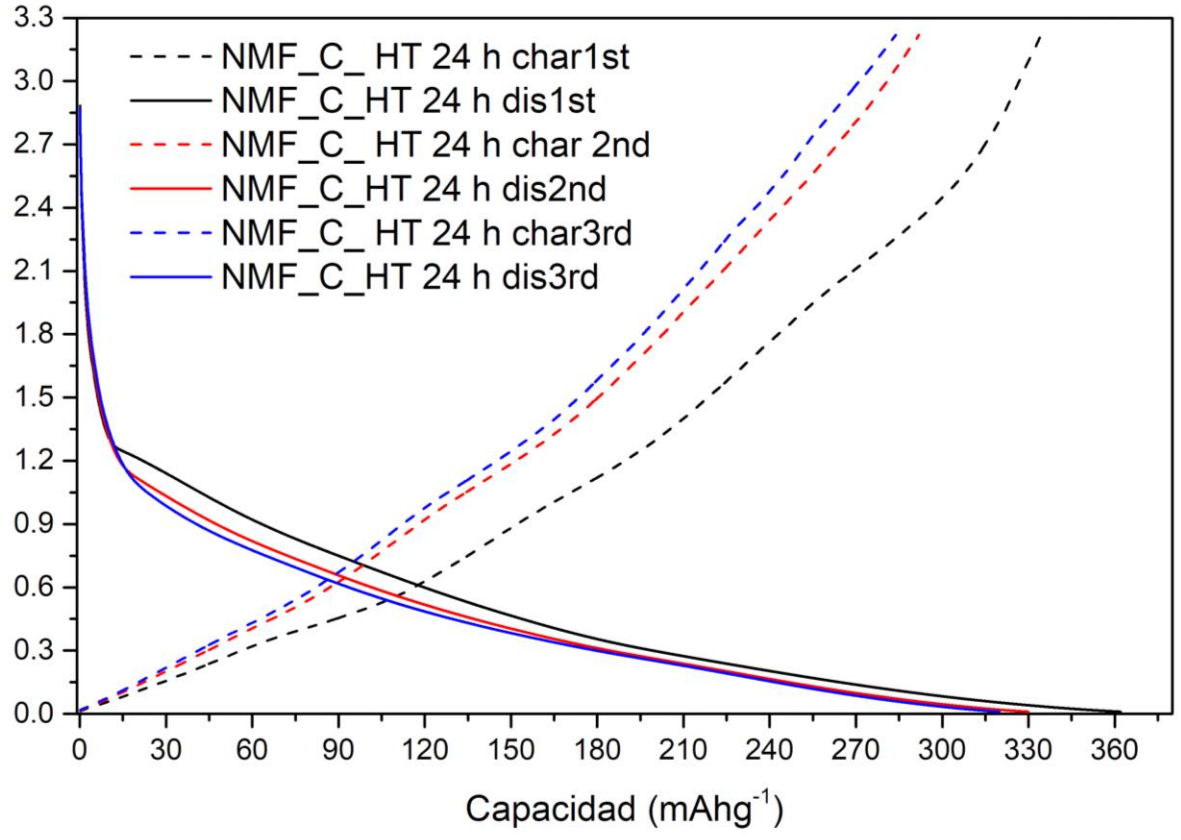
NMF__HT_24h

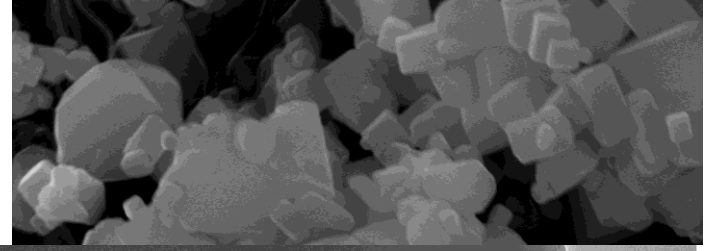


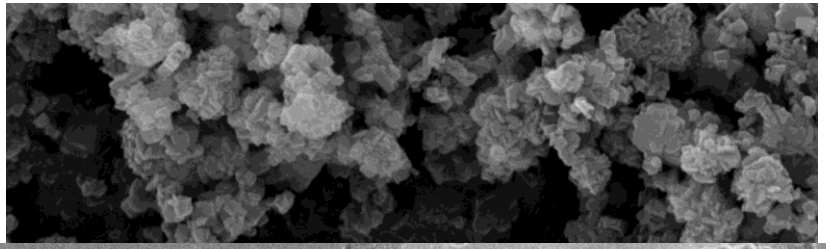
NMF_C_HT_24h

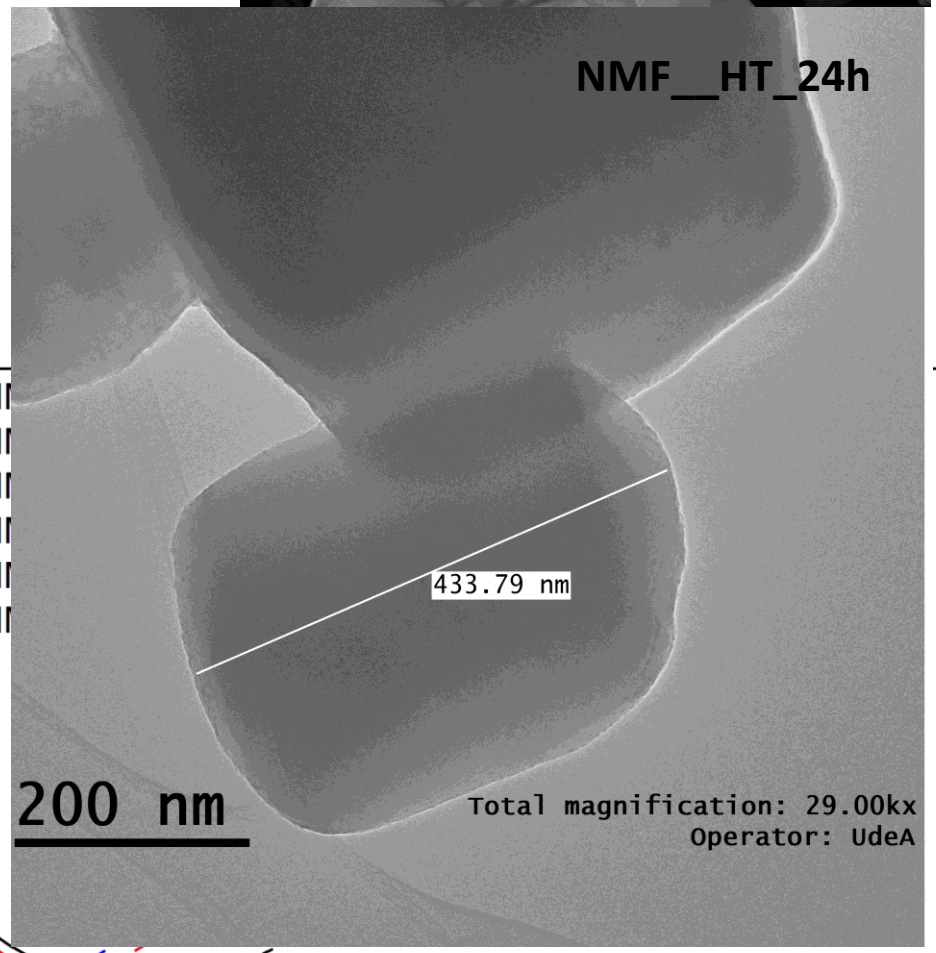


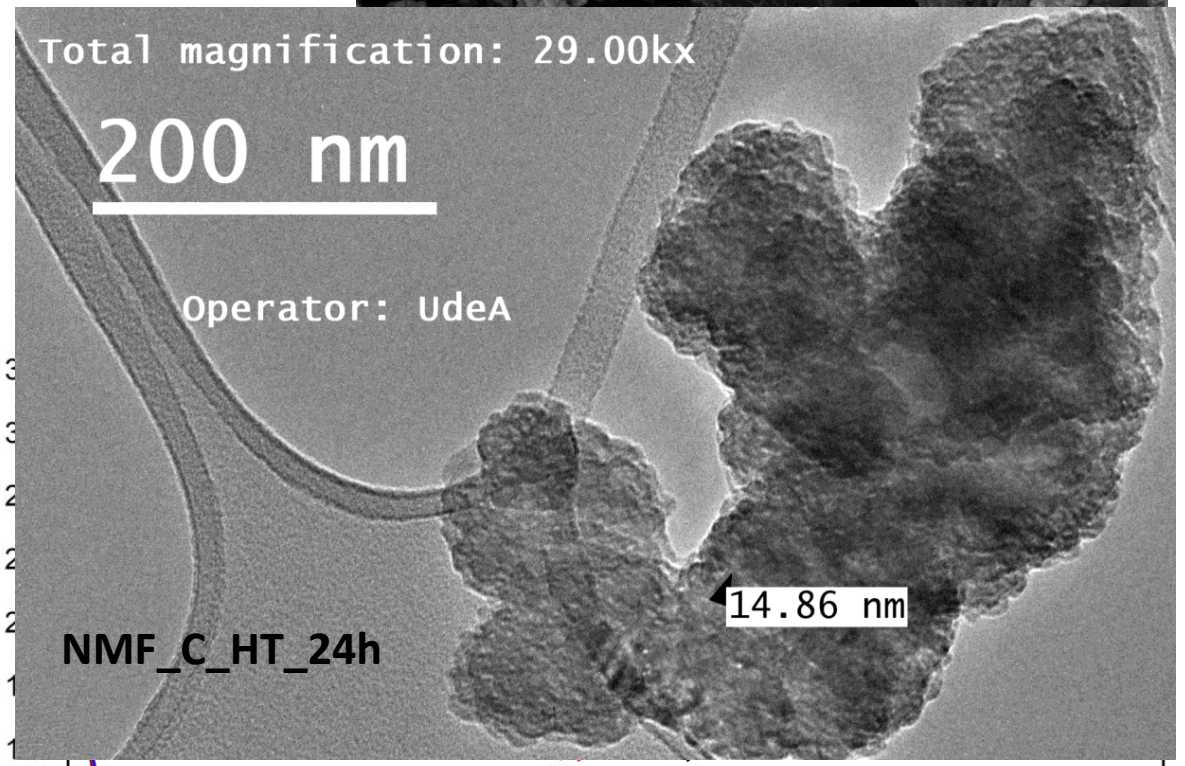








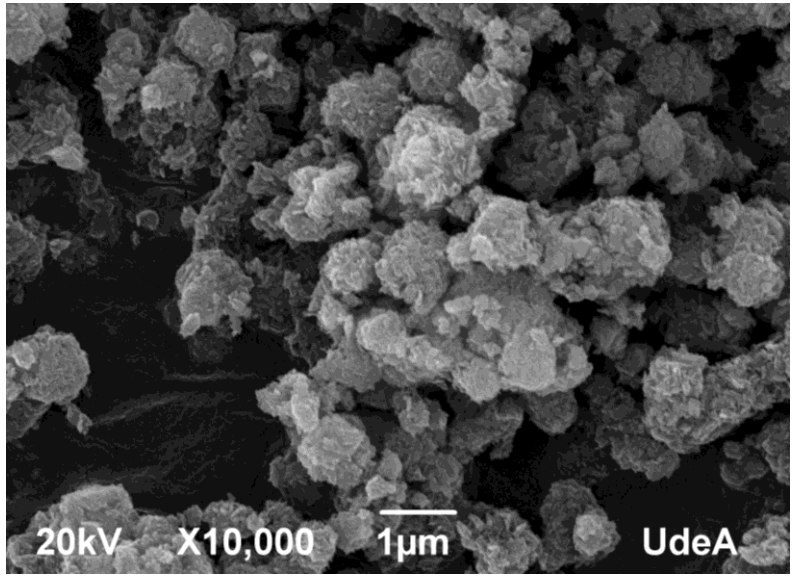

NMF__HT_24h
433.79 nm
200 nm
Total magnification: 29.00kx
Operator: UdeA


Total magnification: 29.00kx
200 nm
Operator: UdeA
14.86 nm
NMF_C_HT_24h

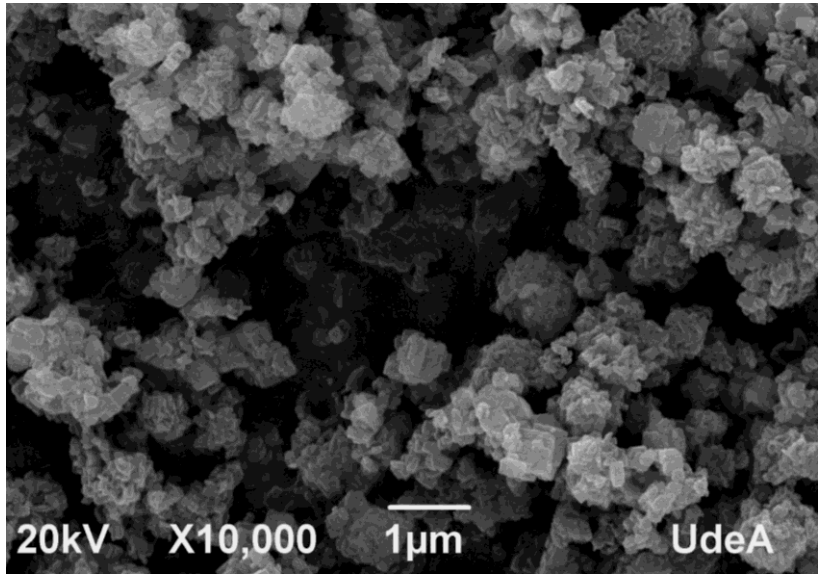
Voltaje (V vs Li/Li+)
Capacidad (mAhg-1)
0
30
60
90
120
150
180
210
240
270
0.0
0.3
0.6
0.9
1.2
1.5
1.8
2.1
2.4
2.7
3.0
3.3

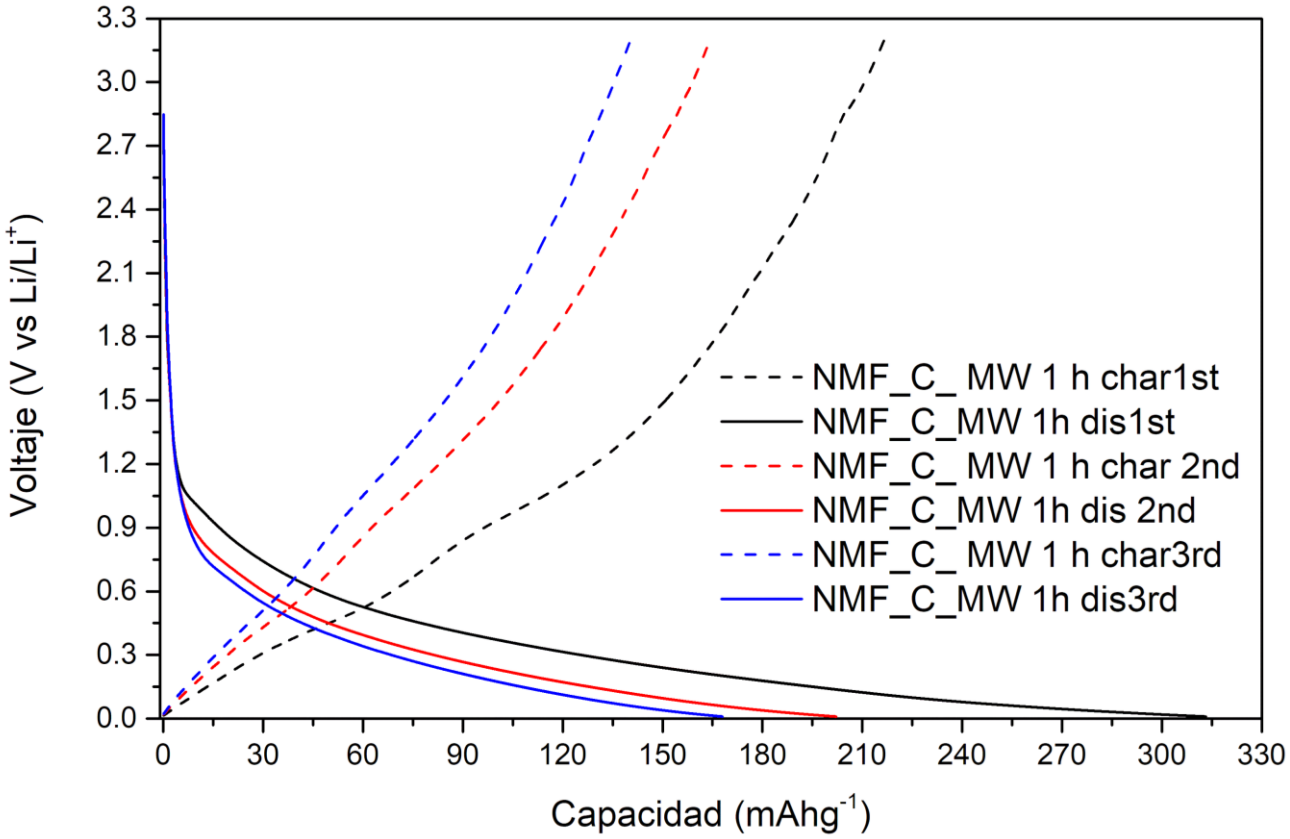
Capacidad (mAhg-1)
0
30
60
90
120
150
180
210
240
270
300
330
360
0.0
0.3
0.6
0.9
1.2

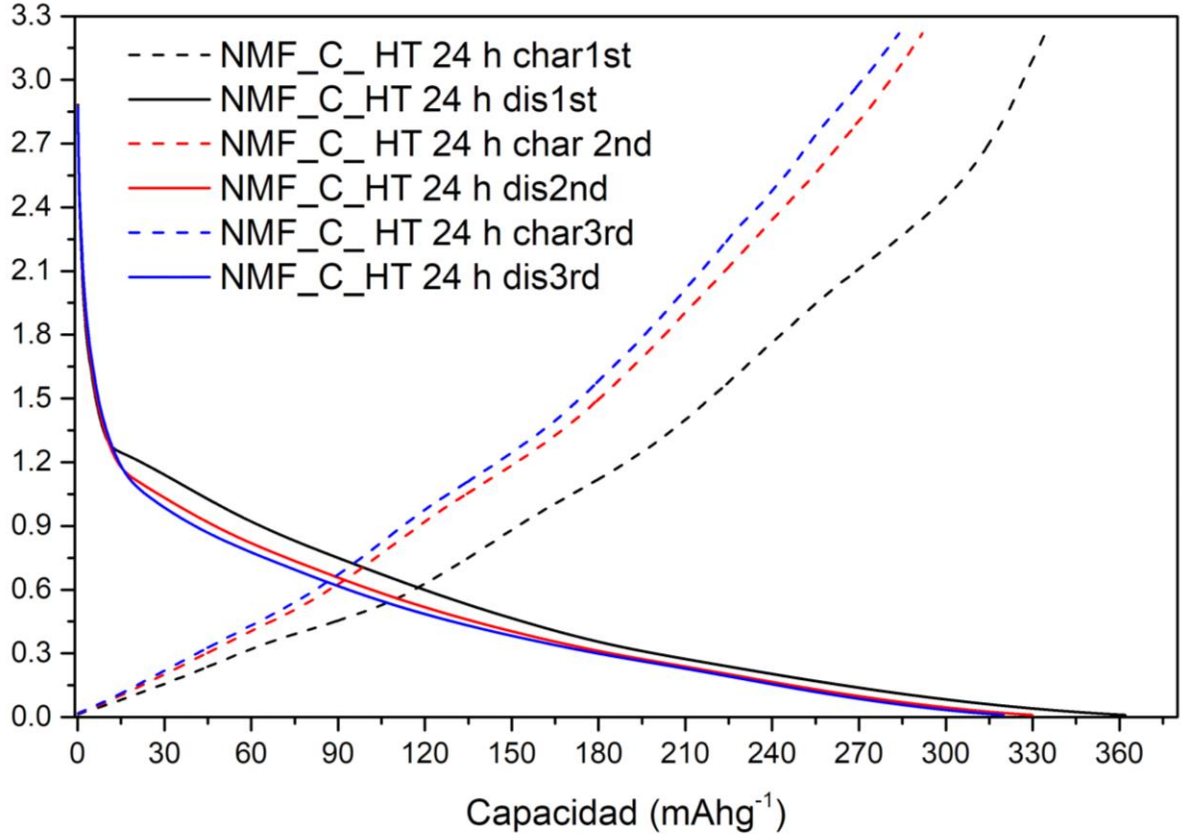
NMF_C_Mw_1h

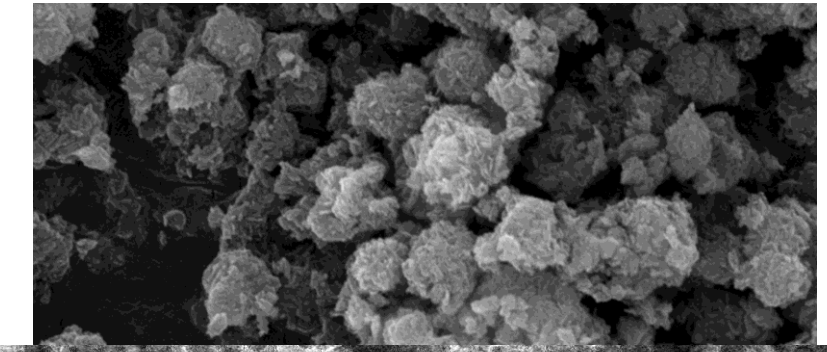


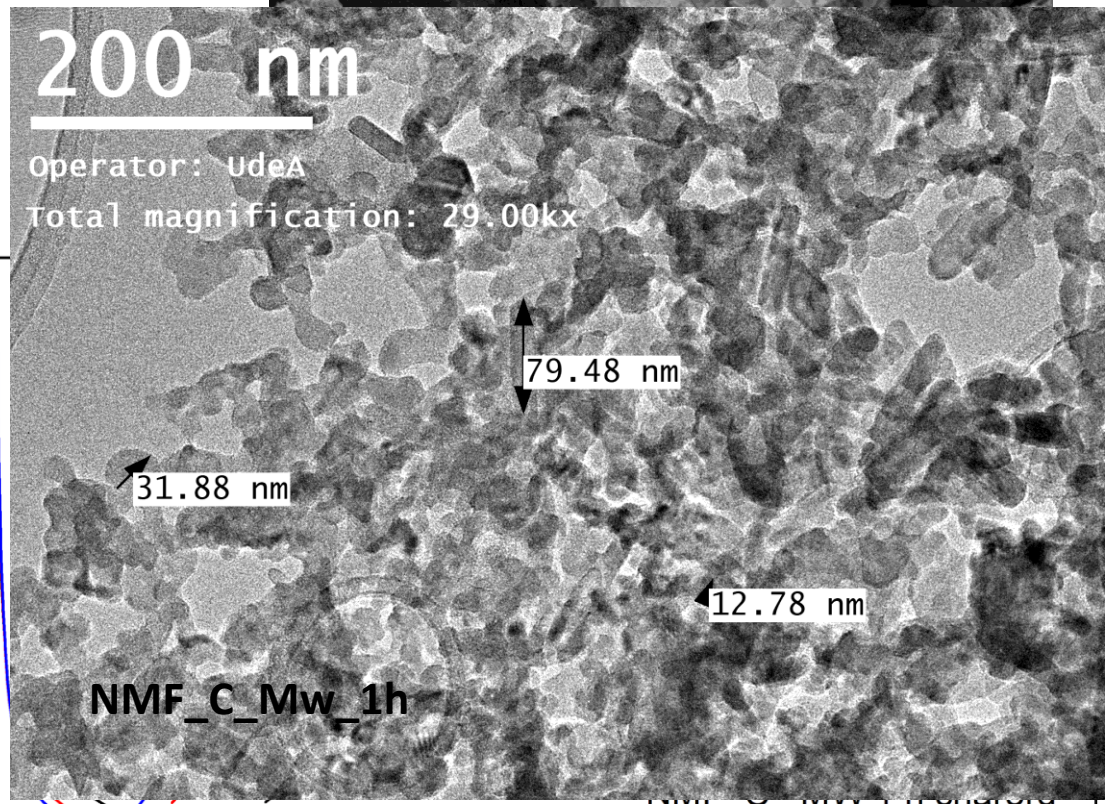
NMF_C_HT_24h

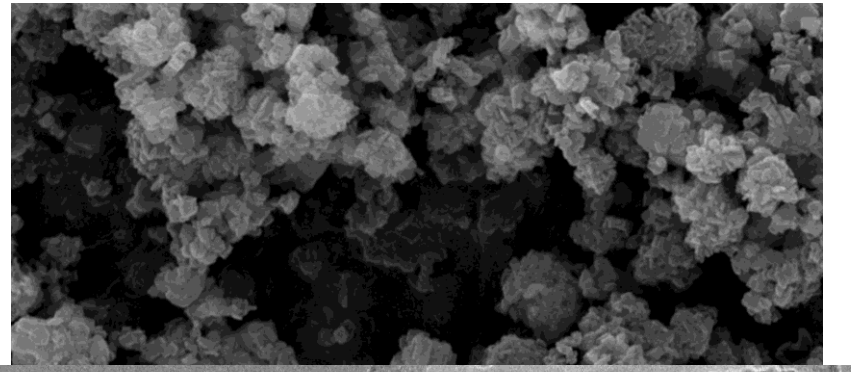


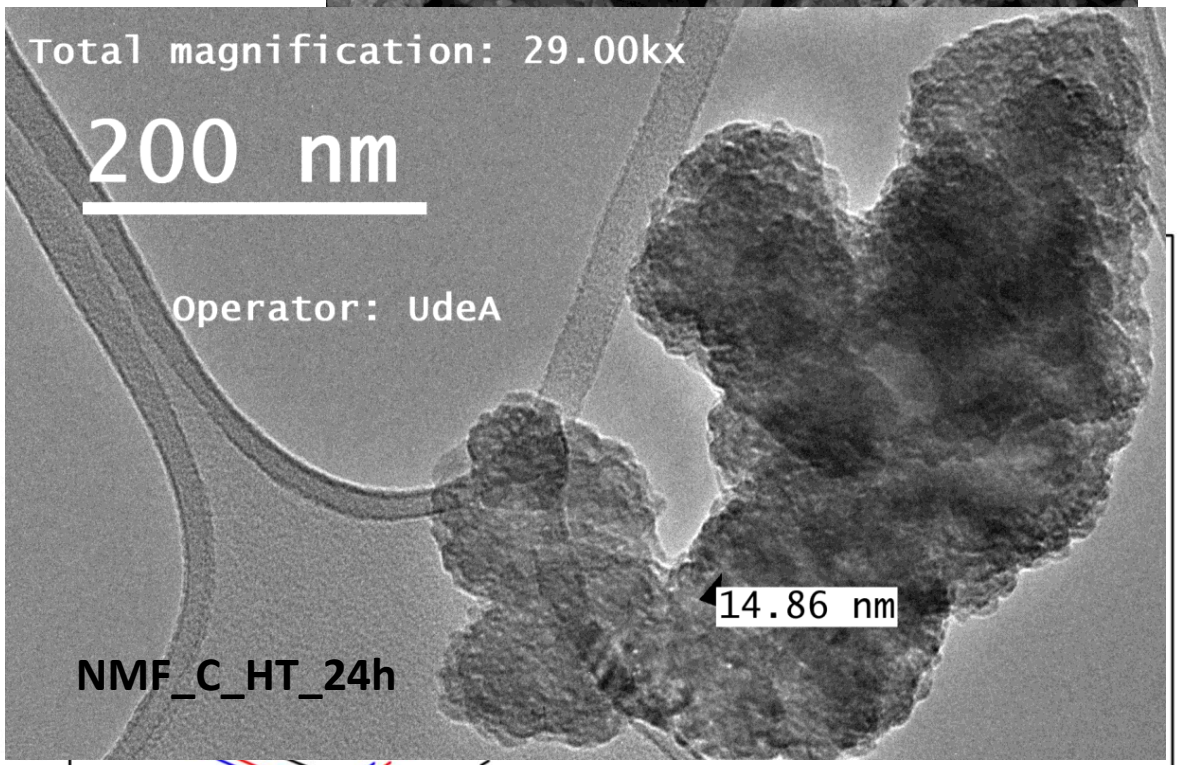




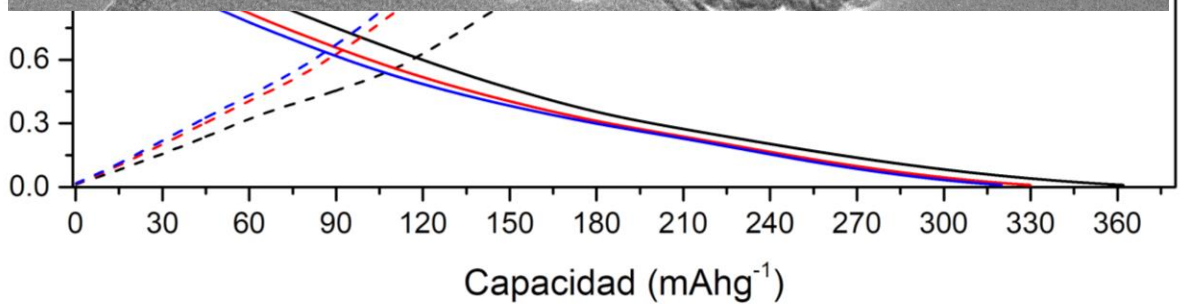



200 nm
Operator: UdeA
Total magnification: 29.00kx
79.48 nm
31.88 nm
12.78 nm
NMF_C_Mw_1h

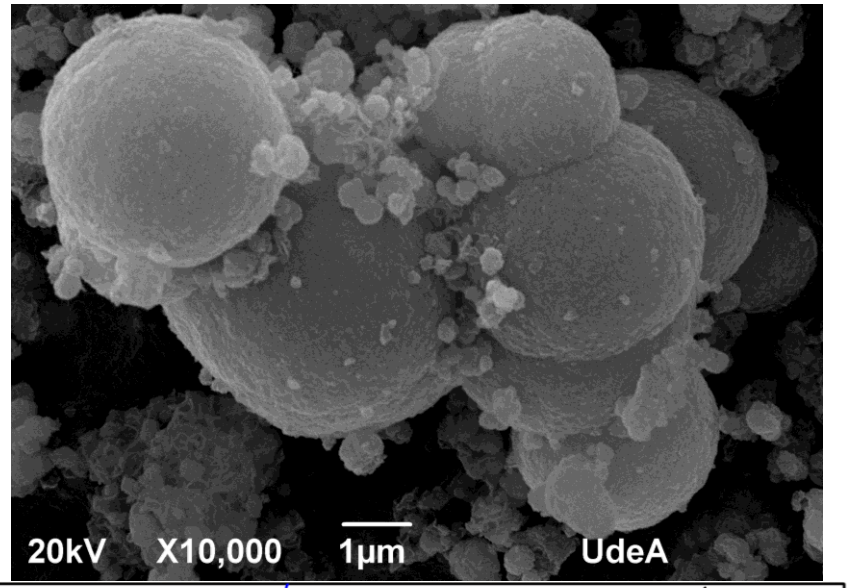


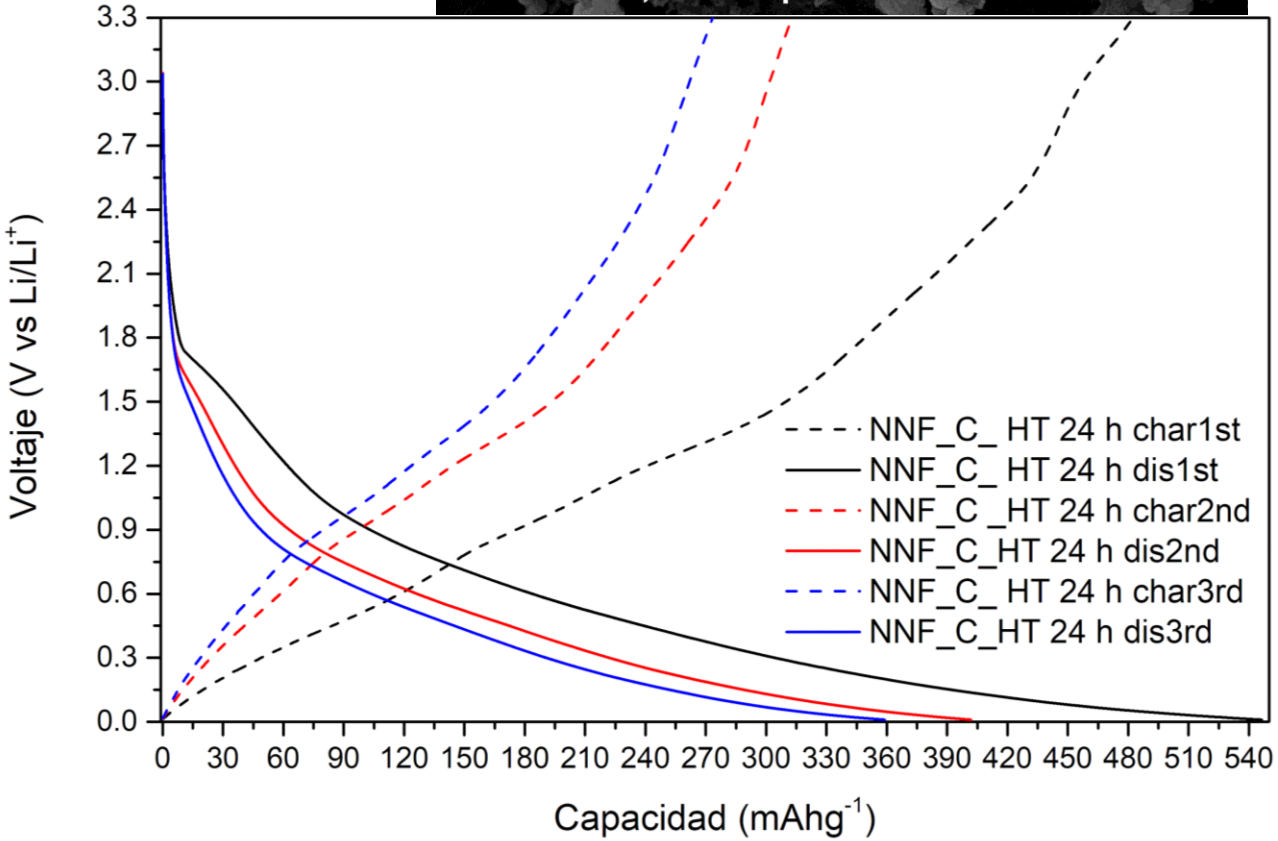

Total magnification: 29.00kx
200 nm
Operator: UdeA
14.86 nm
NMF_C_HT_24h

Voltaje (V vs Li/Li+)
3.3
3.0
2.7
2.4
2.1
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
30
60
90
120
150
180
210
240
270
300
330
Capacidad (mAhg-1)
NMF_C_MW 1h dis3rd

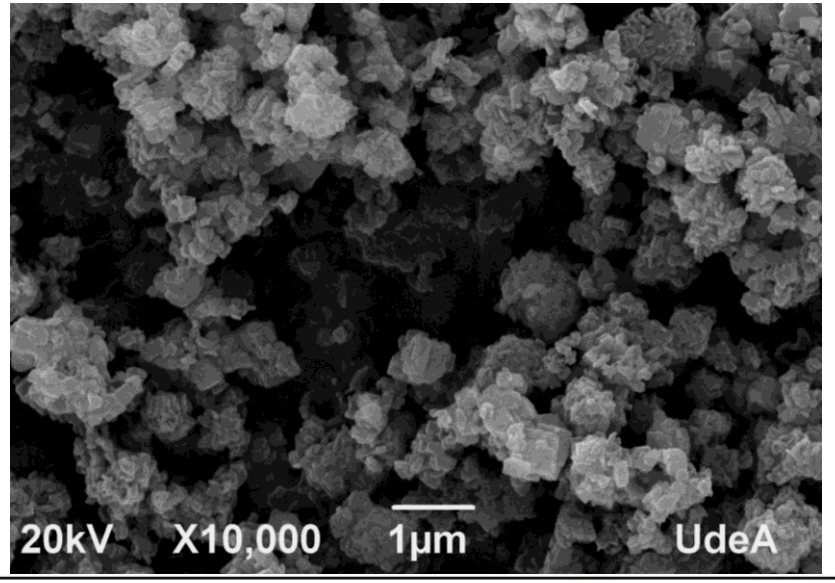

0.6
0.3
0.0
0
30
60
90
120
150
180
210
240
270
300
330
360
Capacidad (mAhg-1)

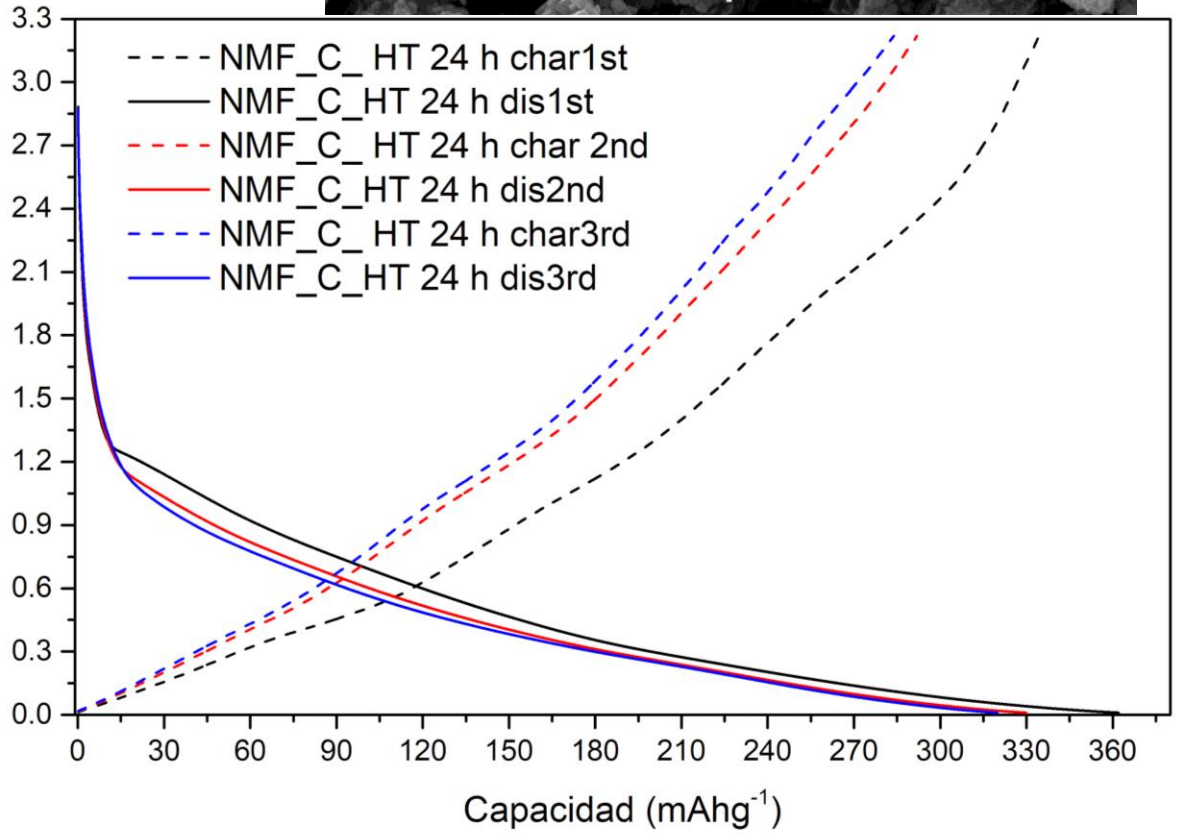
NNF_C_HT_24h

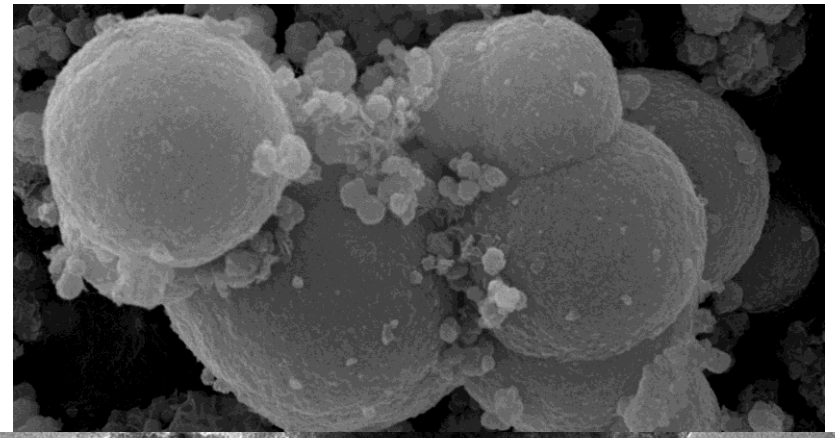


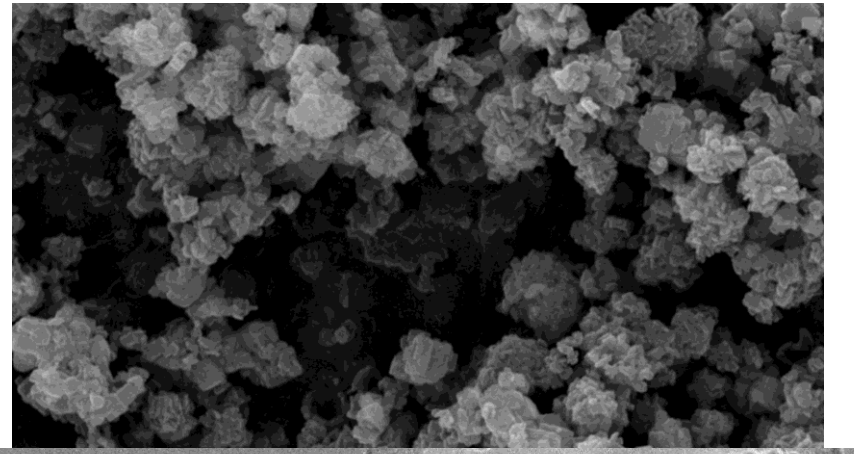


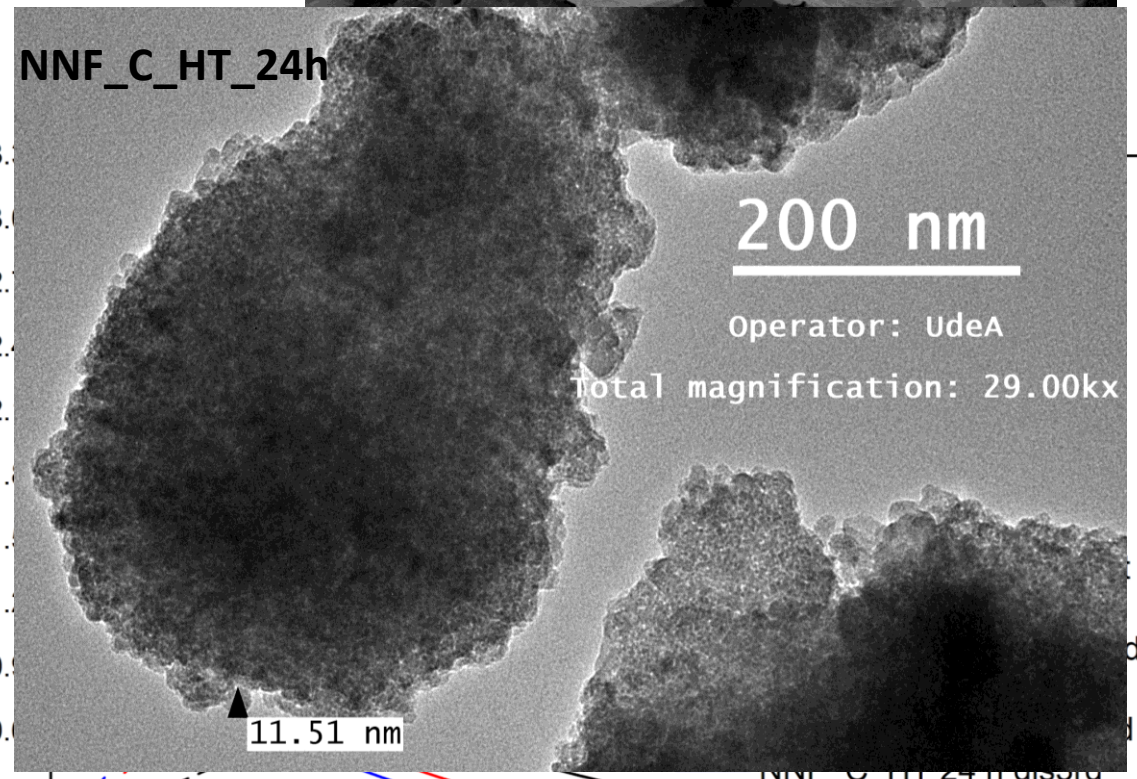
NMF_C_HT_24h

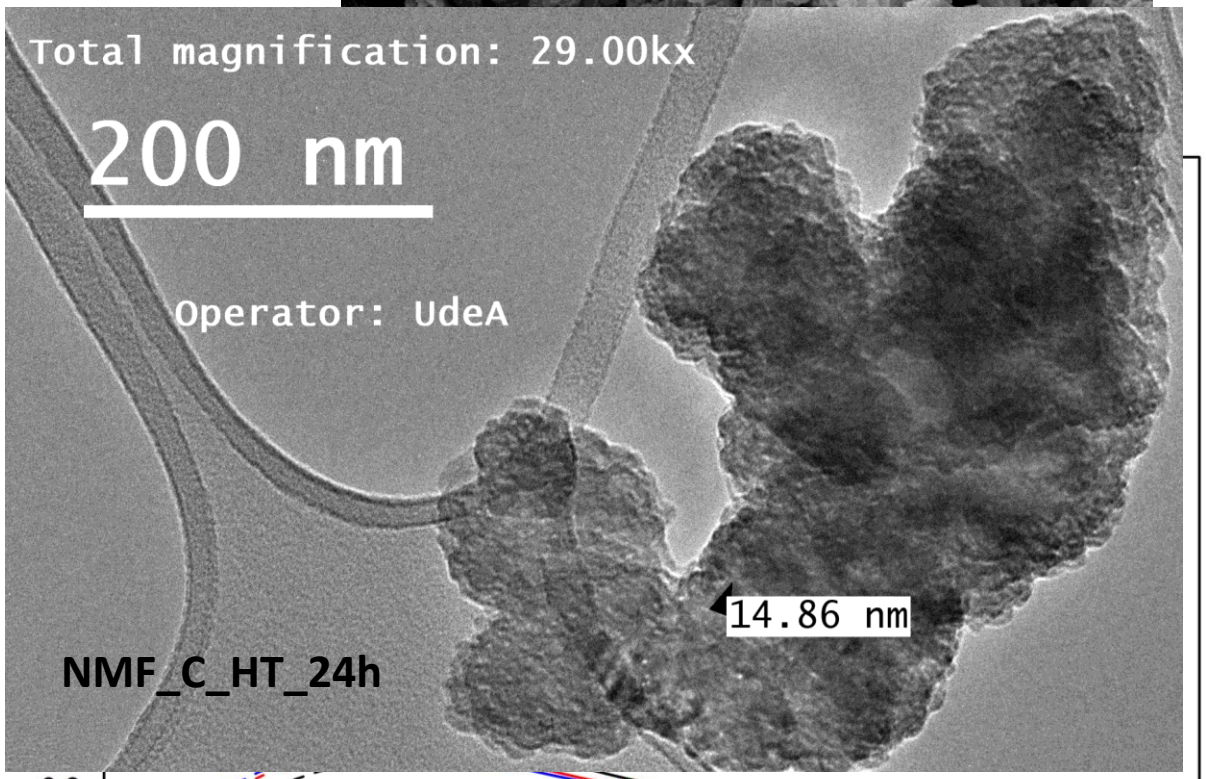






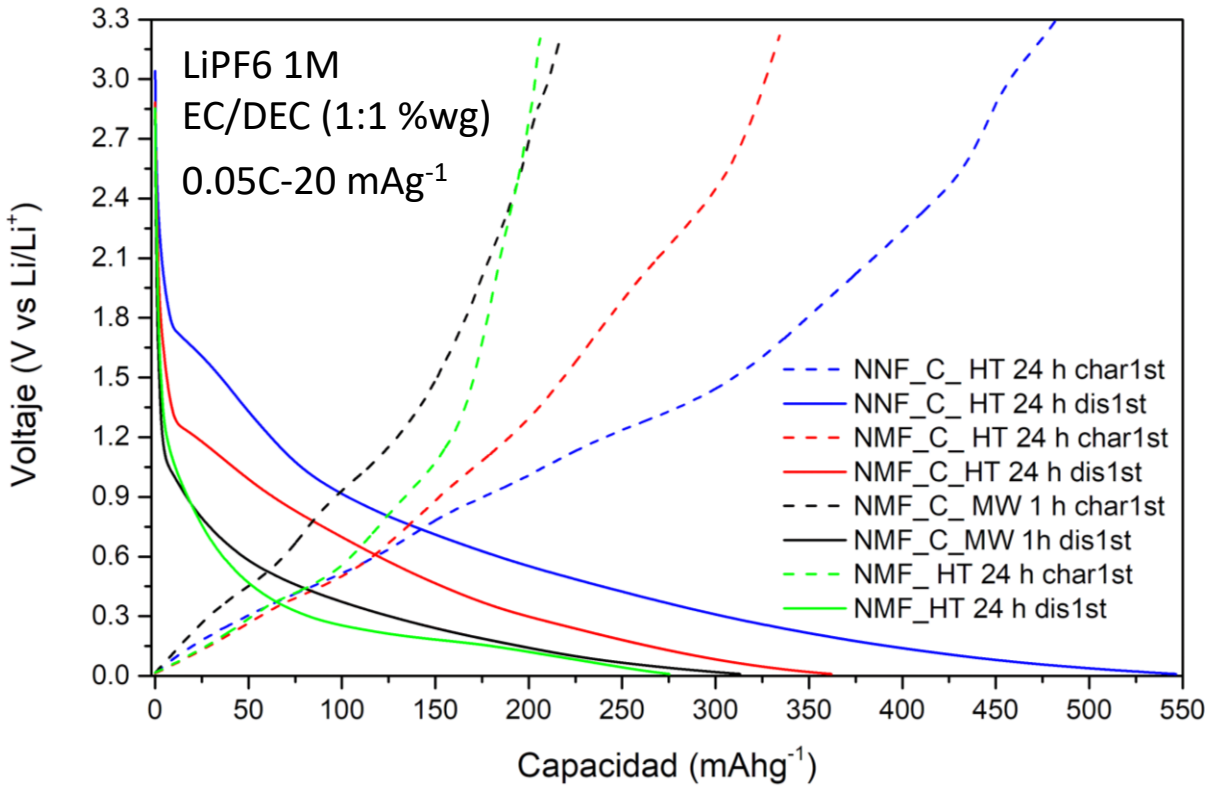


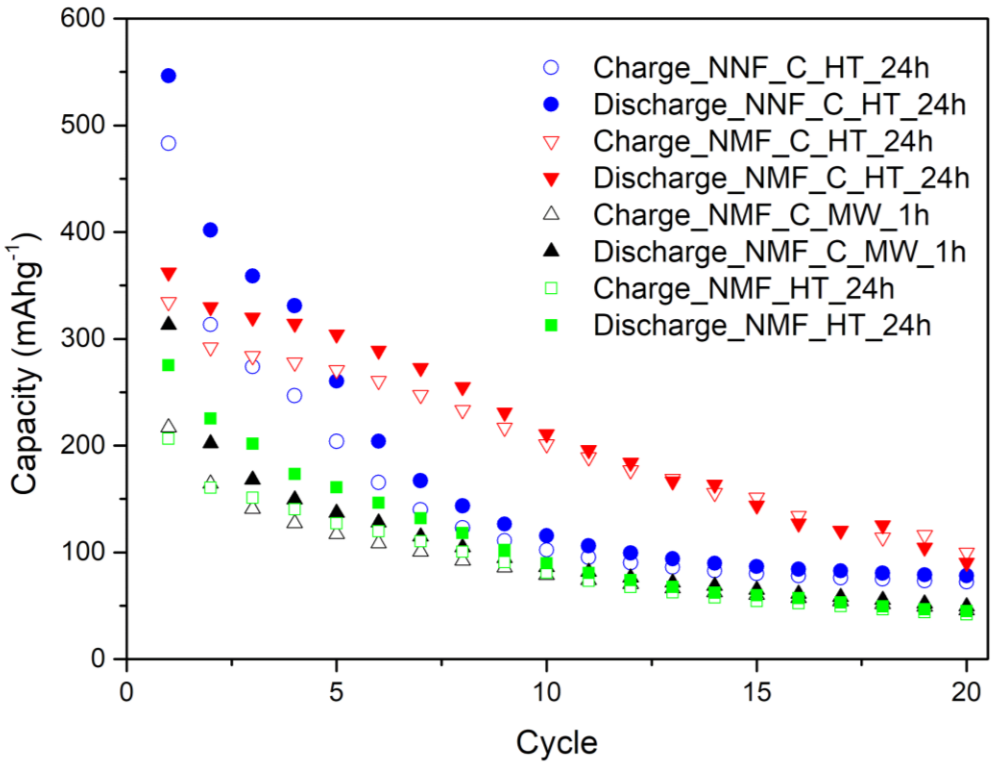

NNF_C_HT_24h
200 nm
Operator: UdeA
Total magnification: 29.00kx
11.51 nm


Total magnification: 29.00kx
200 nm
Operator: UdeA
14.86 nm
NMF_C_HT_24h

Voltaje (V vs Li/Li+)
Capacidad (mAhg-1)
0.0
0.3
0 30 60 90 120 150 180 210 240 270 300 330 360 390 420 450 480 510 540

Capacidad (mAhg-1)
0.0
0.3
0 30 60 90 120 150 180 210 240 270 300 330 360





$NaMnF_3 + 2\,Li \rightarrow Mn + NaF + 2\,LiF$

$\Delta H_{calculated}$

-3.693 eV (-356 kJ mol^{-1})

1.8V

Theoretical capacity of $NaMnF_3$ 397mAhg^{-1}

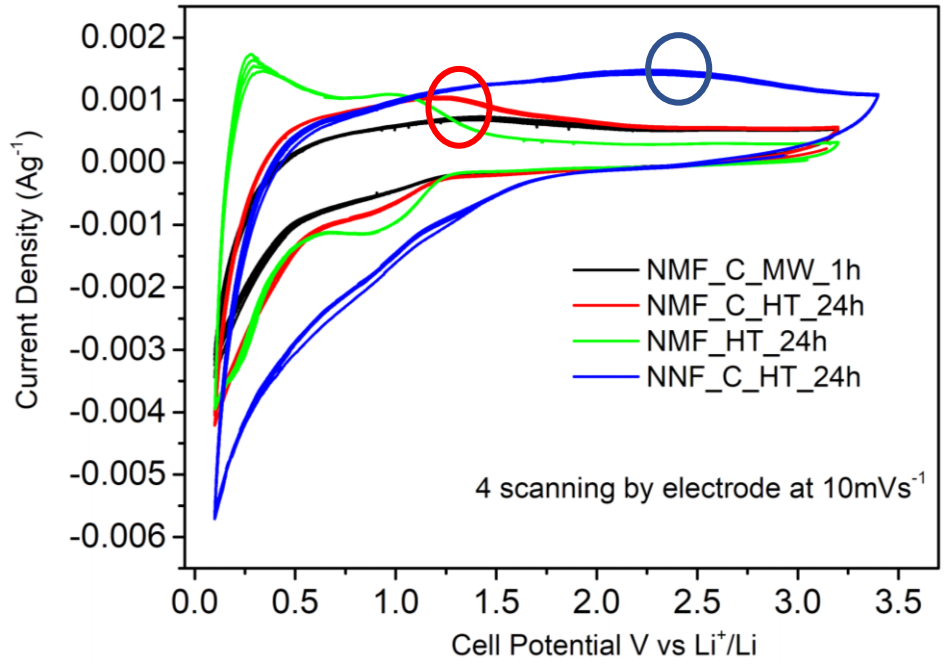
$NaNiF_3 + 2\,Li \rightarrow Ni + NaF + 2\,LiF$

$\Delta H_{calculated}$

-5.610 eV (-541 kJ mol^{-1})

2.8V

Theoretical capacity of $NaNiF_3$ 323mAhg^{-1}



https://materialsproject.org/ Materials Project

Conclusions

- Active material $NaNiF_3$ and $NaMnF_3$ perovskites were obtained and evaluated as anode material of lithium-ion batteries.
- The morphology and electrochemical analysis of the materials were incorporated.
- Capacities up to 560 $mAhg^{-1}$ for $NaNiF_3$ and 360 $mAhg^{-1}$ for $NaMnF_3$ during the first discharge were achieved.

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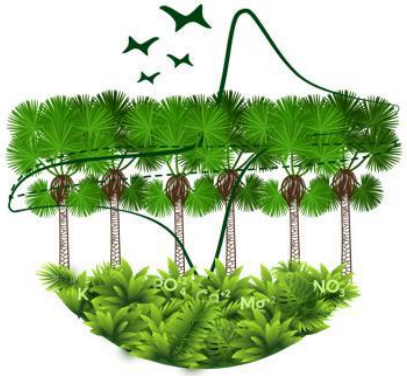

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Liliana T. López Ch., Franklin Jaramillo, Jorge A. Calderón

Thank you

E-mail*: lilianat.lopez@udea.edu.co

Acknowledgements for:

El conocimiento es de todos
Minciencias

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