CONTENIDO

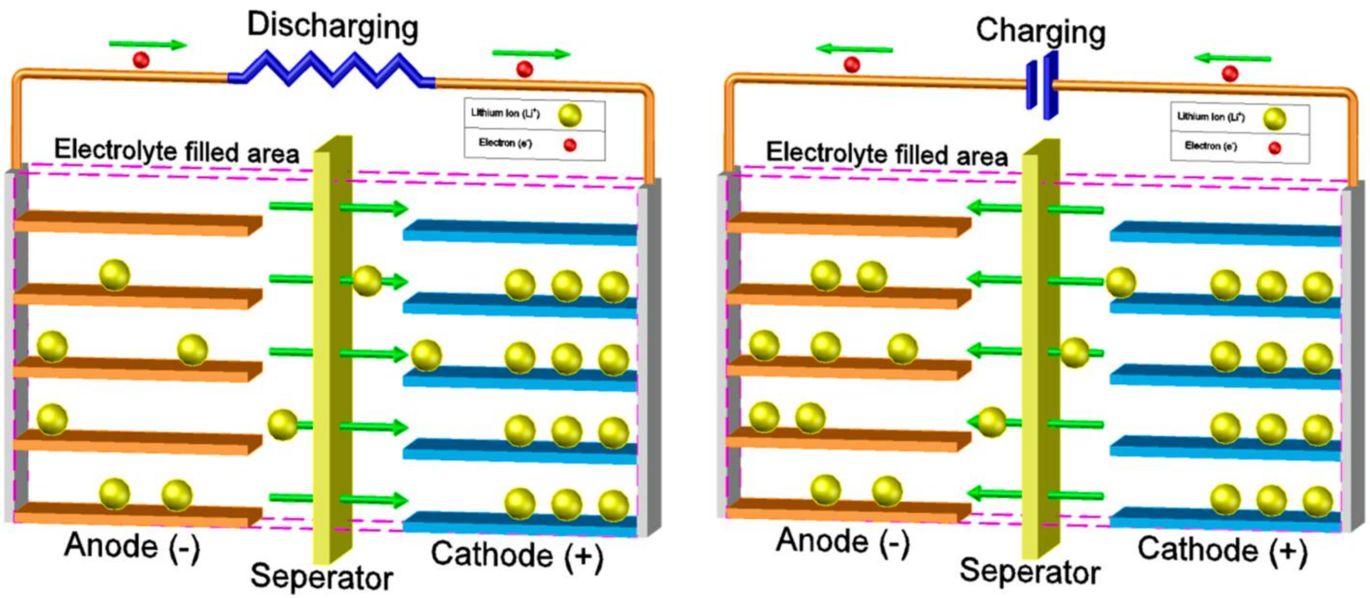
PRACTICA DE ABSORCIÓN DE RAYOS X

ANÁLISIS DE DATOS XANES

- Introducción a los aspectos críticos de las celdas de ion-litio.
- Una perspectiva desde los materiales catódicos: LFP.
- Aprovechamiento de técnicas basadas en rayos X para caracterizaciones químicamente selectivas e in situ / operando
- Determinación del estado de carga en función del potencial en una celda de ion Li de LFP

EXPERIMENTOS CUÁNTICOS II
2025

Félix G. Requejo



Introducción

Producción a escala de celdas de ion-litio

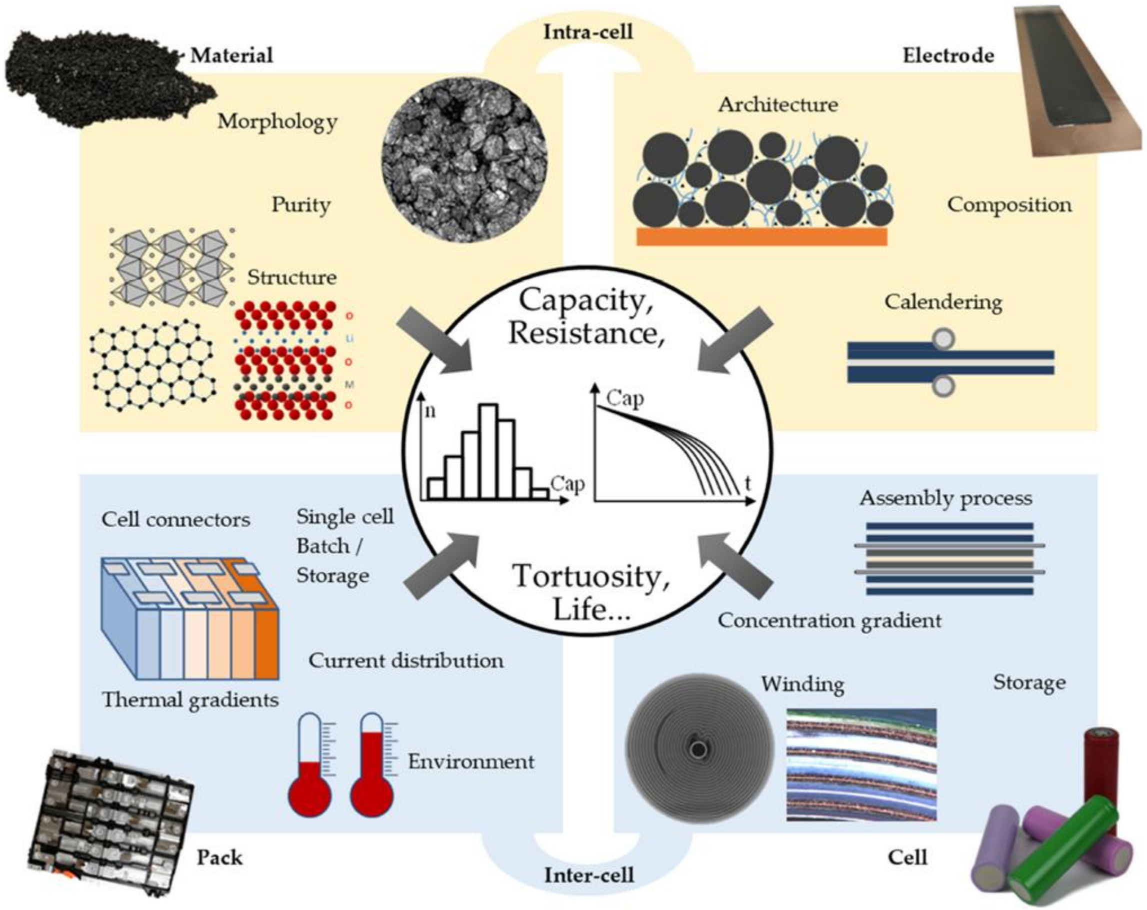
El LFP como material catódico activo

Aditivos de carbono en materiales LFP (cátodo)

Estabilidad estructural y química en LFP durante el ciclado

Lithium-Ion cells at different scales

Intra-cell: active materials, electrolyte, additives
Laboratory scale



Inter-cell: manufacture, CELL array for BATTERY
Industrial scale

Inhomogeneities and Cell-to-Cell Variations in Lithium-Ion Batteries, a Review.
D. Beck et al., Energies 2021, 14, 3276

Intra-cell: active materials, electrolyte, additives

Laboratory scale

Lithium-Ion cells at different scales

Effect of material inhomogeneities
Reversibility/stability
Diffusion, etc
(inter-cell / laboratory)

Impact of heterogeneities in battery pack
(intra-cell / manufacturing)

Inhomogeneities and Cell-to-Cell Variations in Lithium-Ion Batteries, a Review.
D. Beck et al., Energies 2021, 14, 3276

Framework for Analysis of Lithium-Ion Battery Pack Balancing Including Cell Parameter Heterogeneity
P.T. Abadie et al., IFAC PapersOnLine 55-37 (2022) 726–733

→ Characterization with spatial resolution:
What role can it play?

Inter-cell: manufacture, CELL array for BATTERY

Industrial scale

Inhomogeneities and Cell-to-Cell Variations in Lithium-Ion Batteries, a Review.
D. Beck et al., Energies 2021, 14, 3276

Intra cell: active materials

Why LFP?

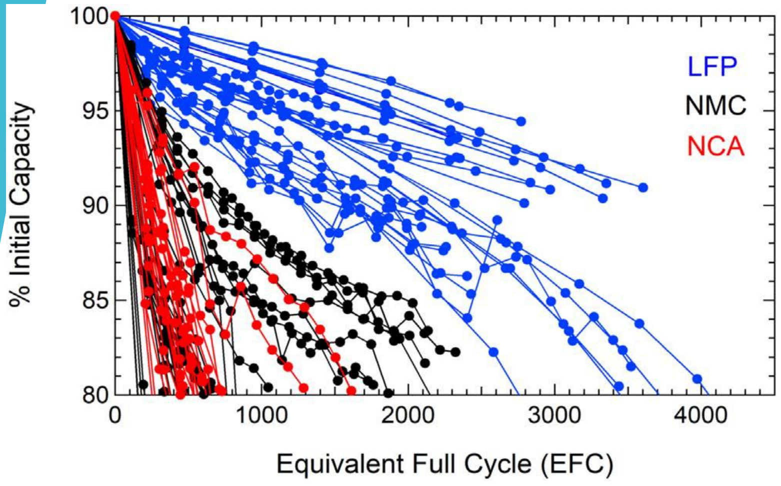
LFP/rGO for higher performance

LFP ($LiFePO_4$)

NCA ($LiNi_xCo_yAl_{1-x-y}O_2$)

NMC ($LiNi_xMn_yCo_{1-x-y}O_2$)

Discharge capacity retention for all LFP (blue), NMC (black), and NCA (red) cells relative to the initial capacity of each individual cell.



LFP cells had the **highest cycle lifetime** across all conditions, but this performance gap was reduced when cells were compared according to the **discharge energy throughput**.

Commercial 18650-format **lithium-ion battery** manufacturer- specified operating bounds.

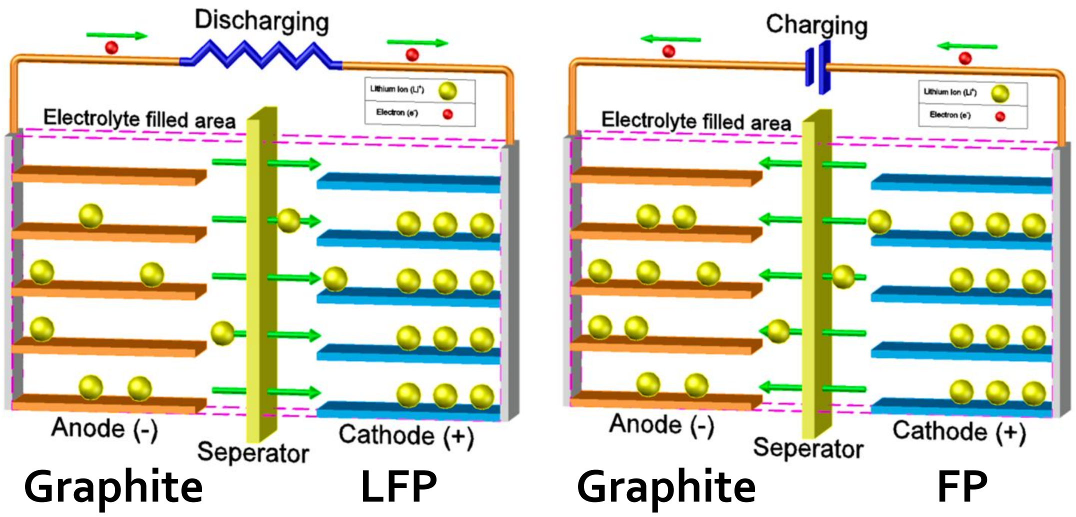
Battery	LFP	NCA	NMC
Nominal Capacity (Ah)	1.1	3.2	3
Nominal Voltage (V)	3.3	3.6	3.6
Voltage Range (V)	2 to 3.6	2.5 to 4.2	2 to 4.2
Max Discharge Current (A)	30	6	20
Acceptable Temperature (°C)	−30 to 60	0 to 45	−5 to 50
Nominal Mass (g)	39	48.5	47

ADDITIONAL ADVANTAGES:

- **More environmentally friendly**: LFP batteries don't use the same toxic chemicals and harmful heavy metals such as cobalt or nickel like other types of batteries.
- **Safety**: thermal runaway. LFP possesses higher thermal stability compared to cobalt-based chemistries.
- **Economy**: raw materials available in the region (comparative advantage for our region).

Degradation of Commercial Lithium-Ion Cells as a Function of Chemistry and Cycling Conditions
Yuliya Preger et al. 2020 J. Electrochem. Soc. 167 120532

Intra cell: active materials



Why LFP?

LFP/rGO for higher performance

LFP ($LiFePO_4$)

FP ($FePO_4$)

LFP cells had the **highest cycle lifetime** across all conditions, but this performance gap was reduced when cells were compared according to the **discharge energy throughput**.

Strategies to improve diffusion rate of lithium ions (Li+) and the electronic conductivity of LFP:

a) Add conductive/coated conductive carbon,
b) Doping of metal anions/cations and
c) Reduce particle size

Recent Report on the Hydrothermal Growth of $LiFePO_4$ as a Cathode Material
D. Vernardou, Coatings 2022, 12(10), 1543

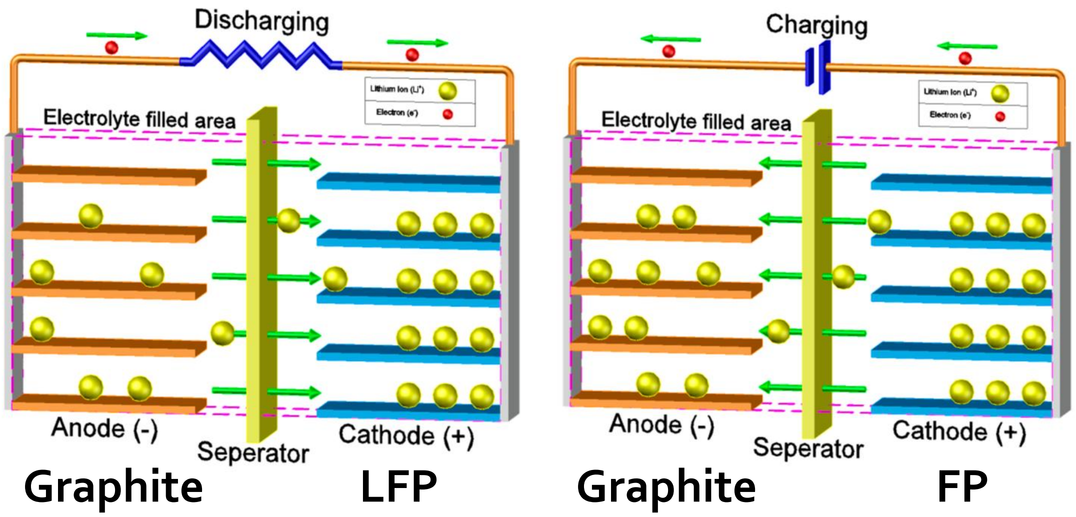
Intra cell: active materials

Why LFP?

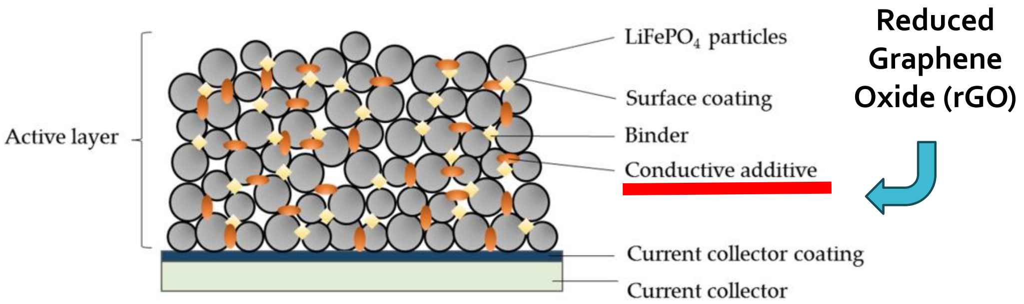
LFP/rGO for higher performance

LFP (LiFePO4)

FP (FePO4)



GOAL: include (reduced) graphene oxide (GO) during hydrothermal synthesis to improve conductivity (and discharge energy throughput)



Advantages of the hydrothermal process: high material stability, eco-friendliness, low production costs and material abundance, easily tuned to modify lithium iron phosphate characteristics such as structure, morphology and particle size.

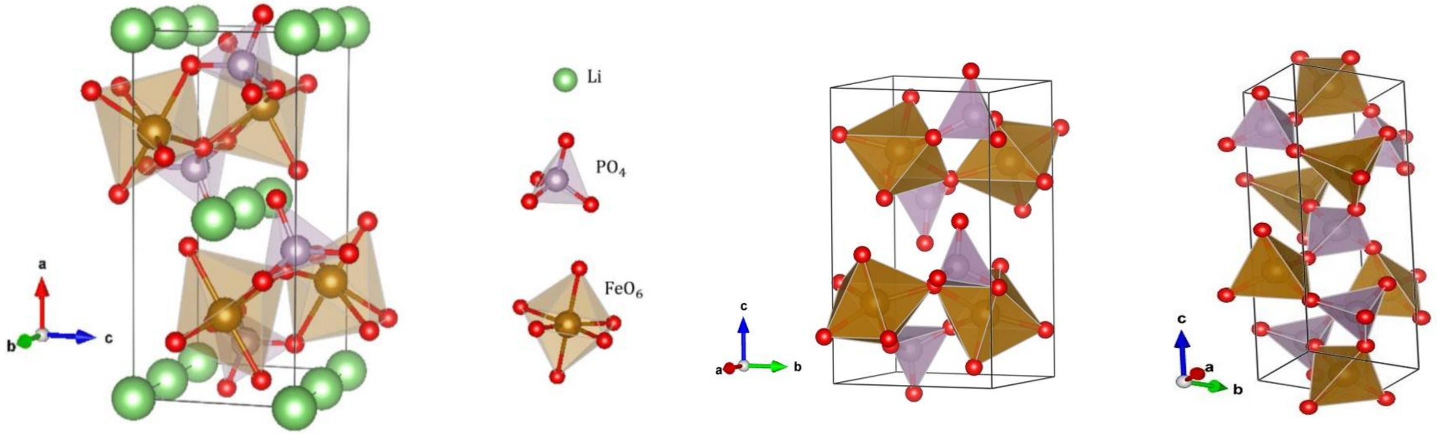
Recent Report on the Hydrothermal Growth of LiFePO4 as a Cathode Material
D. Vernardou, Coatings 2022, 12(10), 1543

Phase transition mechanism:

LFP active materials

Structural issues (XRD)

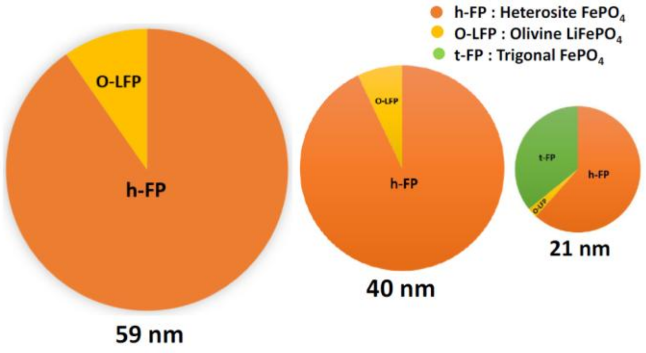
LFP (triphylite LFP) FP (heterosite & trigonal FP)



(O) (H) (T)

Local structure and electronic structure of LiFePO4 as a cathode for lithium-ion batteries
F. Astuti et al 2021 J. Phys.: Conf. Ser. 1951 012007

Characteristic behavior in the structural properties of heterosite $FePO_4$ shows a strong dependency on the crystallite size which is correlated with the change in the chemical



Structural heterogeneity
(different phase distribution according to crystallite size)

Nanosized FP: observed local lattice distortion decrease in the level of covalency between the Fe-3d and O-2p states. Further, such structural possess advantages of on the transport properties.

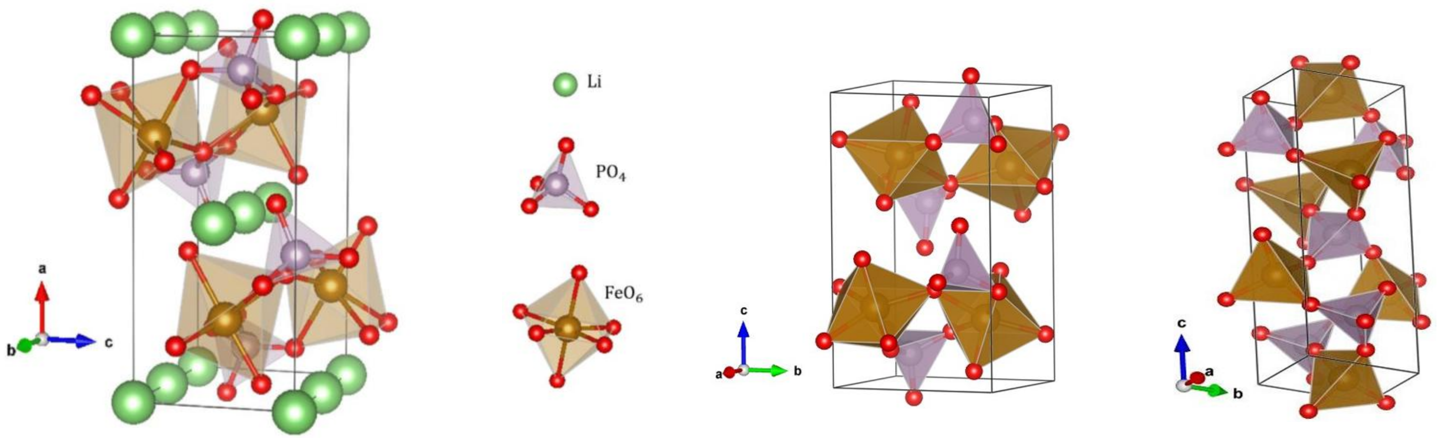
***Effect of Crystallite Size on the Phase Transition Behavior of Heterosite* FePO4**
A. Banday et al., Phys. Chem. Chem. Phys., 2020,22, 15478-15487

Phase transition mechanism:

LFP active materials

Structural issues (XRD)

LFP (triphylite LFP) ⟺ FP (heterosite & trigonal FP)

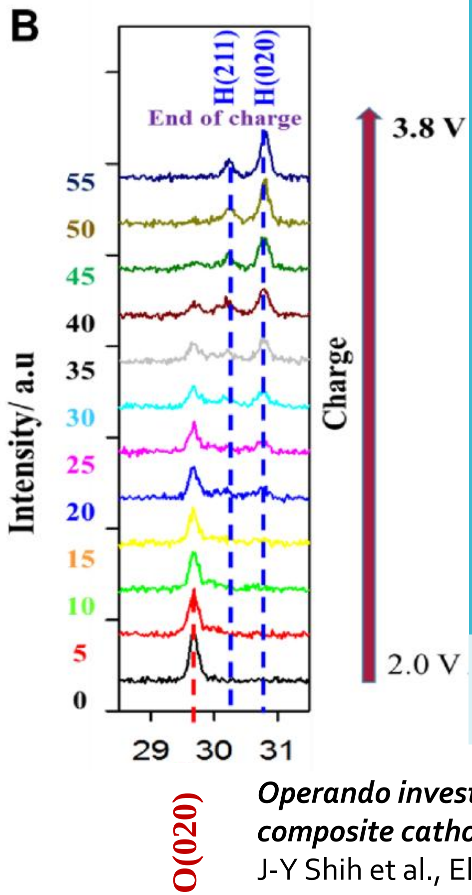


(O) (H) (T)

Local structure and electronic structure of LiFePO4 as a cathode for lithium-ion batteries
F. Astuti et al 2021 J. Phys.: Conf. Ser. 1951 012007

XRD to "in situ" following phase transformation:

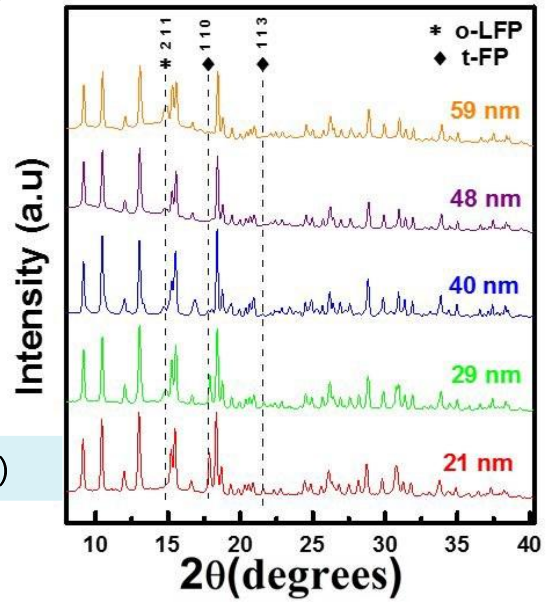
- Lithiation degree
- Type of phase
- Stability



LPF (O): O(020) plane (2θ = 29.7°)
FP (H): H(020) plane (2θ = 30.9°)

Operando investigation on the fast two-phase transition kinetics of LiFePO4/C composite cathodes with carbon additives for lithium-ion batteries
J-Y Shih et al., Electrochimica Acta 419 (2022) 140356

FP (T): H(110) plane (2θ = 17.8°)

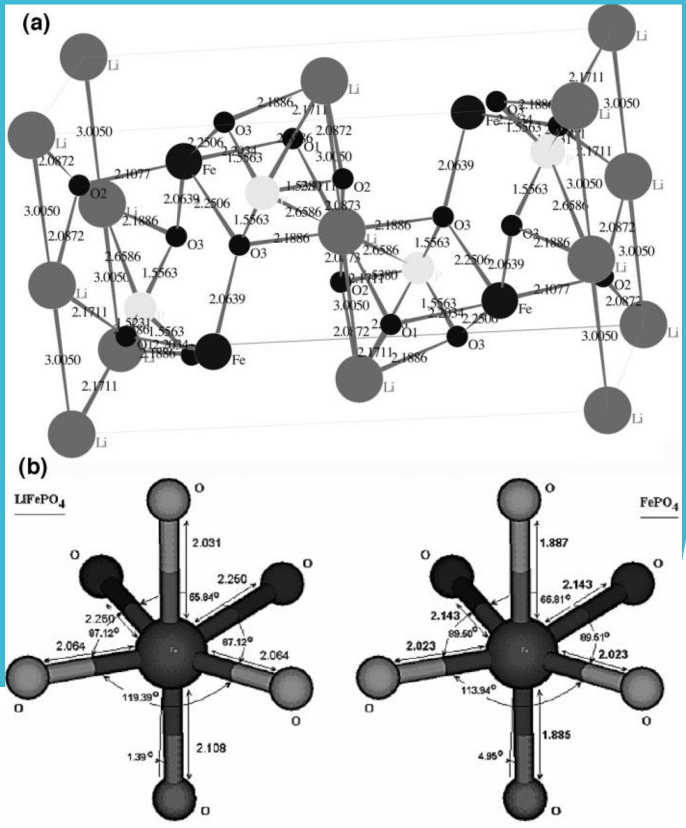


Effect of Crystallite Size on the Phase Transition Behavior of Heterosite FePO4
A. Banday et al., Phys. Chem. Chem. Phys., 2020,22, 15478-15487

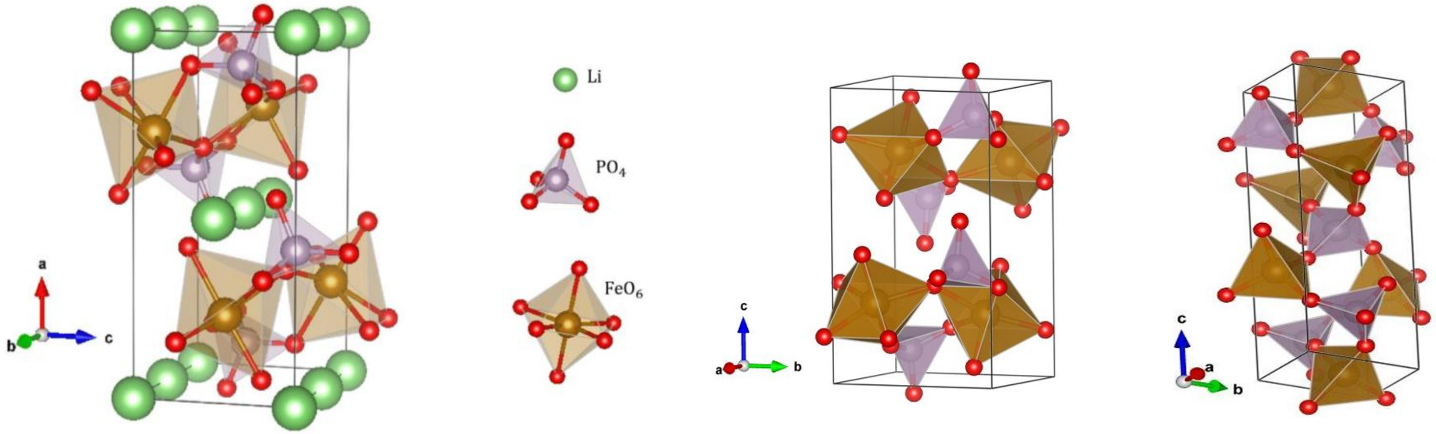
Phase transition mechanism:

LFP active materials

Chemical issues (XAFS)

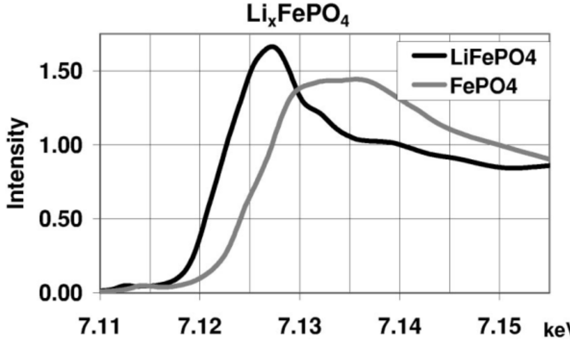


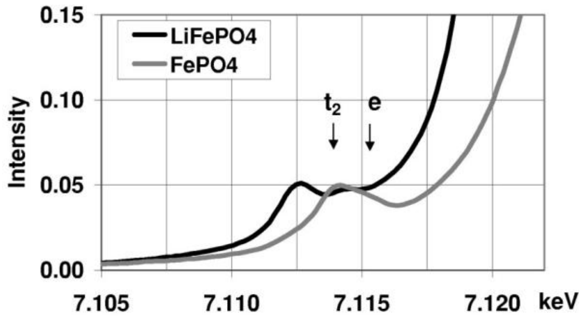
LFP (triphylite LFP) ⟷ FP (heterosite & trigonal FP)



(O) (H) (T)

Local structure and electronic structure of $LiFePO_4$ as a cathode for lithium-ion batteries
F. Astuti et al 2021 J. Phys.: Conf. Ser. 1951 012007



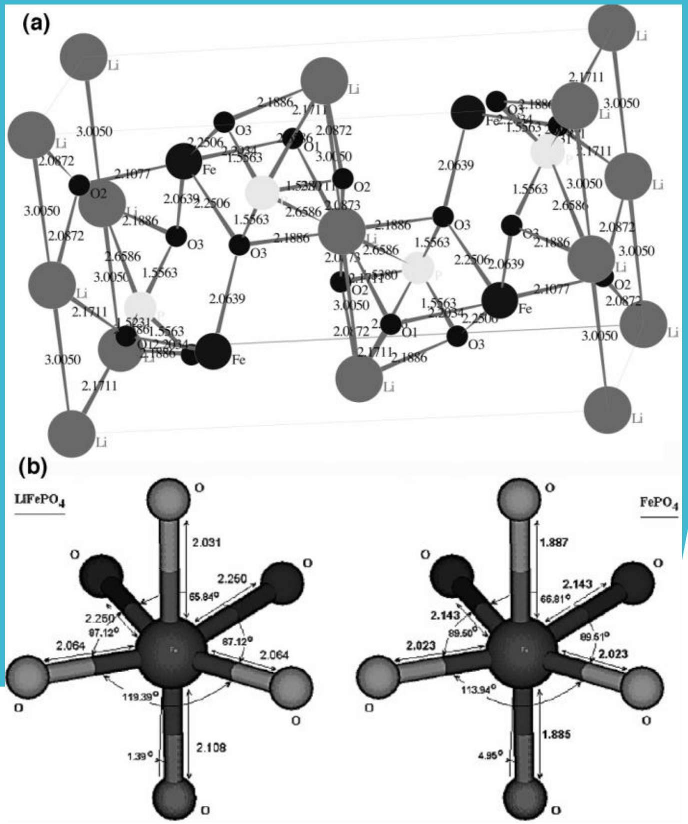


Synchrotron X-Ray Absorption Study of $LiFePO_4$ Electrodes
O. Haas et al., Journal of The Electrochemical Society, 152 (1) A191-A196 (2005)

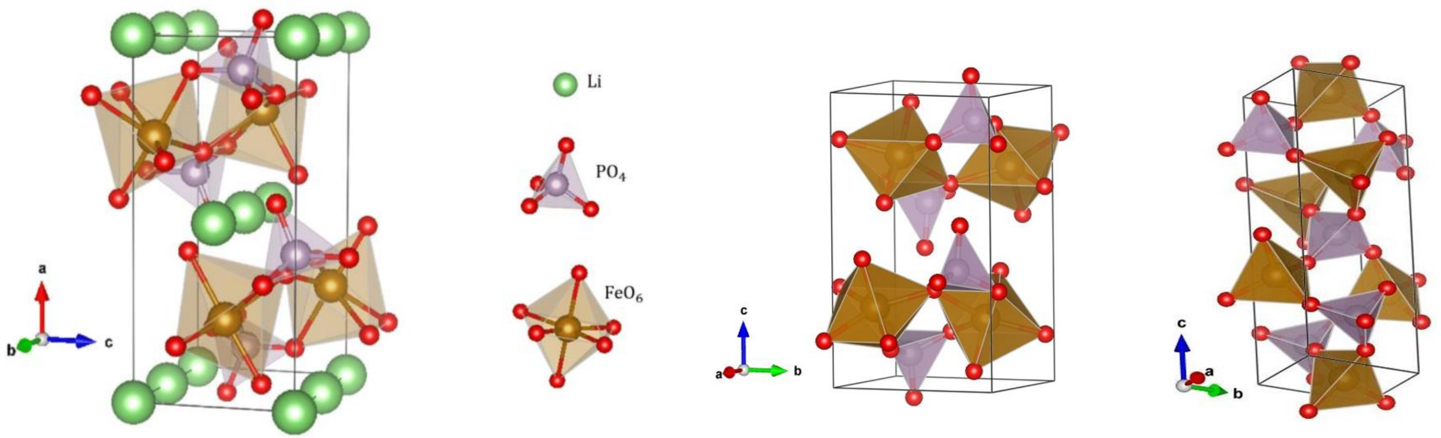
Phase transition mechanism:

LFP active materials

Chemical issues (XAFS)



LFP (triphylite LFP) FP (heterosite & trigonal FP)



(O) (H) (T)

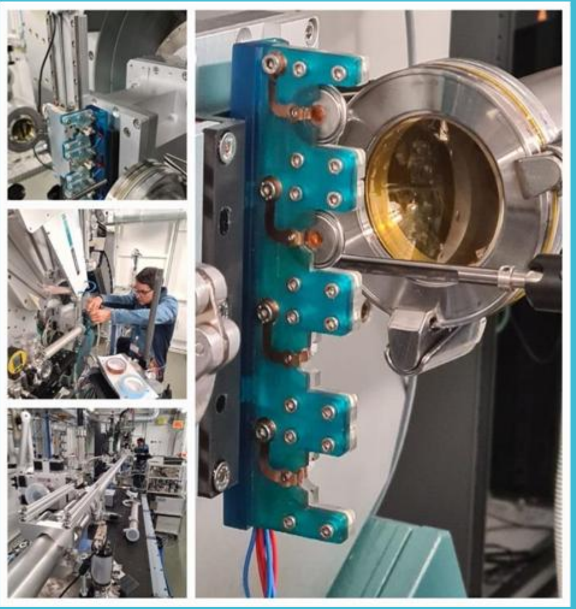
Local structure and electronic structure of $LiFePO_4$ as a cathode for lithium-ion batteries
F. Astuti et al 2021 J. Phys.: Conf. Ser. 1951 012007

XANES to "in situ" following phase transformation:

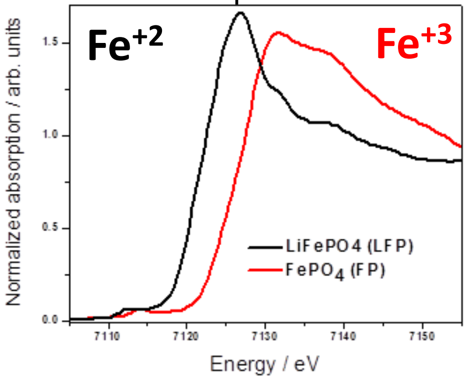
- State of charge (SOC)
- Local structure transformation (even at amorphous phases)
- Stability

Results:
Fe K-XANES

ALBA Synchrotron (NOTOS beamline)

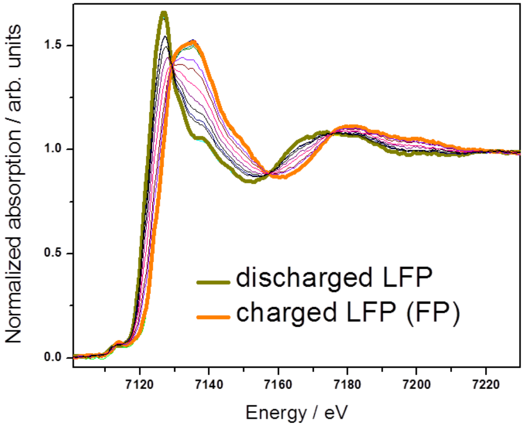


Reference compounds

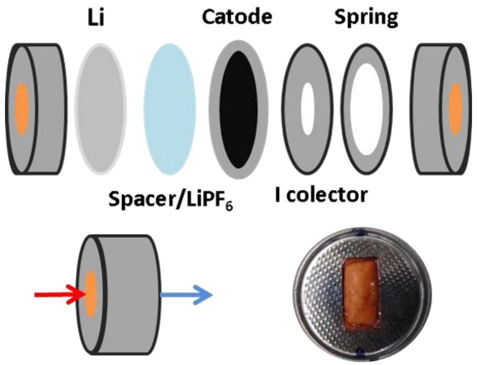


Fe oxidation

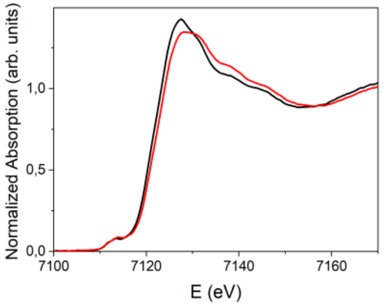
DISCHARGE

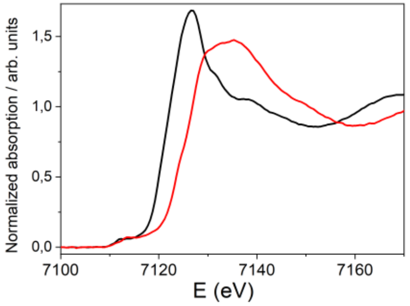


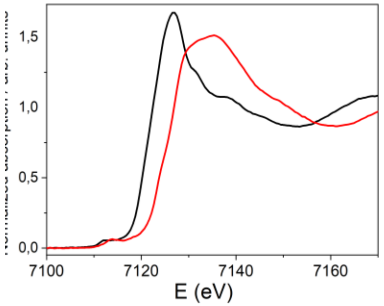
CHARGE



Button (coin) cell







LFP

LFP - GO

LFP - HRTGO

70/80 mA.h / g → 140/150 mA.h / g

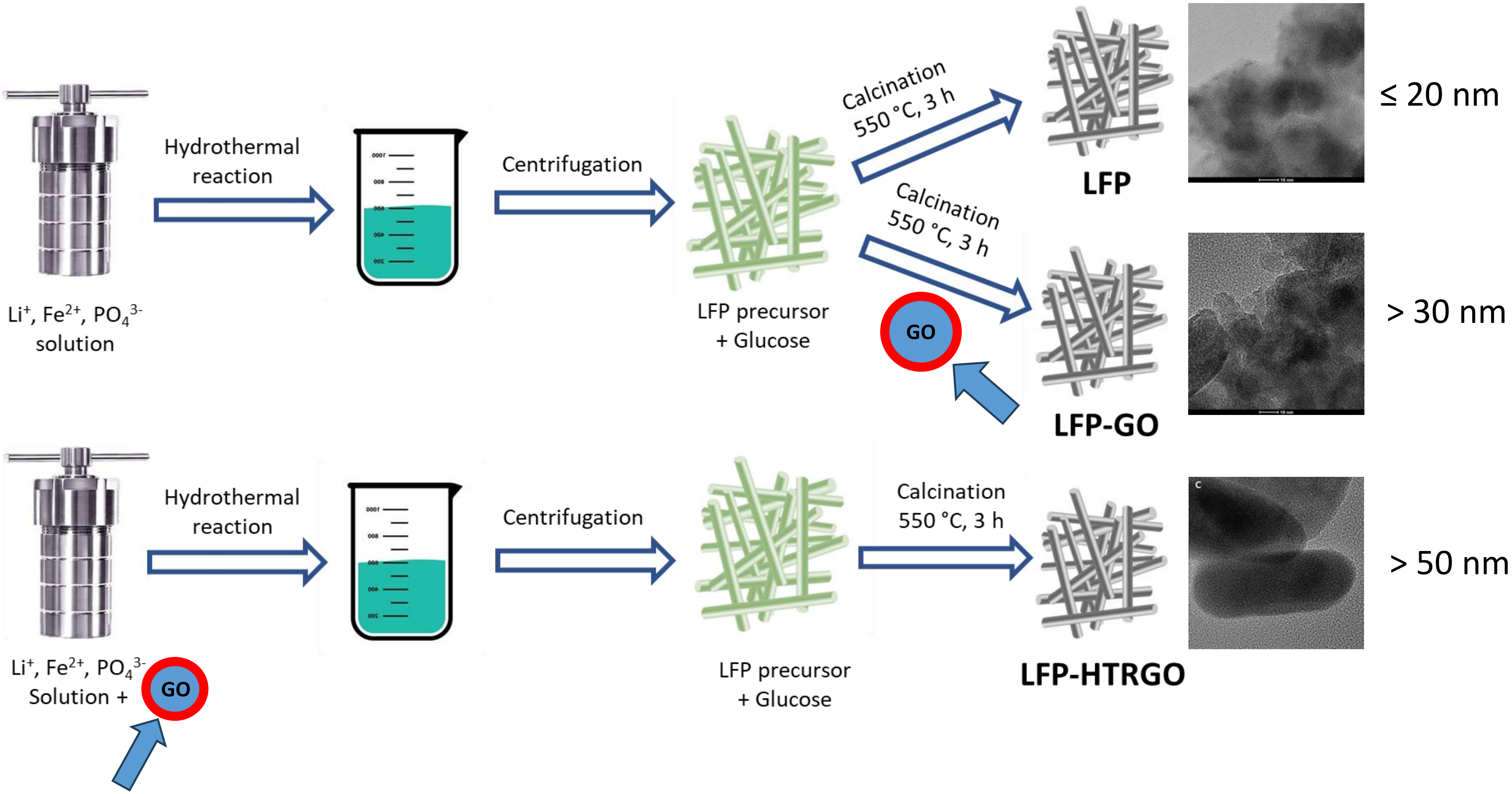
Degree of oxidation/reduction obtained by from energy edge shifting at XANES spectra.

LFP-HTRGO	% Fe^{+2}	% Fe^{+3}
Pristine	90	10
Charged	22	78
Discharged	88	12

FIN

LFP-based electrodes

Synthesis



Enhancement of LiFePO4 cathodic material through incorporation of reduced graphene oxide via a simple two-step procedure.
M.P. Quiroga Argañaraz, K. Jori, J.M. Ramallo López, A. Visintin, F.G. Requejo, M.G. Ortiz
Journal of Physics and Chemistry of Solids, 2024, 112353. doi: 10.1016/j.jpcs.2024.112353