



Impact of synthesis techniques on the structure and performances of LiFePO_4 powders

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Why LiFePO₄ ?

One of the most promising cathode materials for lithium ion batteries with wide applications from portable electronics to hybrid electric vehicles.

The benefits of using LiFePO₄ are: excellent cycle life, high structural stability, low cost and environmental friendliness.

Lithium iron phosphate can utilize one lithium ion per formula unit which leads to the theoretical capacity of 170 mAh/g.



The main obstacle in reaching theoretical capacity is its low electronic and/or ionic conductivity.

There are several possible means to overcome this main obstacle in reaching theoretical capacity: by decreasing the particle size, by coating the particles with electronically conductive agent such as carbon, and by selective doping with supervalent cations.



Outline

- **Description of several synthesis techniques to obtain olivine-type LiFePO_4 powders starting from the same iron precursor, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.**
- **Particle morphology comparison envisaged by scanning electron microscopy.**
- **Comparison of structural and microstructural properties of synthesized powders by using XRPD data.**
- **Investigation of electrochemical lithium intercalation/deintercalation in terms of galvanostatic charge/discharge tests.**
- **Final conclusion about the impact of different synthesis techniques on the properties of LiFePO_4 powders.**



Synthesis techniques:

Solid state reaction

pure LiFePO_4

Ultrasonic spray pyrolysis

composite of LiFePO_4 and carbon

Sonochemical activation

composite of LiFePO_4 and carbon

Precipitation in molten stearic acid

composite of LiFePO_4 and carbon



Synthesis of pure LiFePO_4

Solid state reaction

Li_2CO_3 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{HPO}_4$ in a molar ratio 1:2:2 mixed, ground and calcined

T = 800°C, in argon for 3 hours + reduction with Ar/H₂ (3:1)

Synthesis of composite LiFePO_4 and carbon

Ultrasonic spray pyrolysis

Aqueous solution of LiNO_3 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_3PO_4 , in a molar ratio 1:1:1 and sucrose

Ultrasound frequency 1.7 MHz

$T = 800^\circ\text{C}$

carrier gas: argon, flow rate 20 l/h

No additional heat treatment



Synthesis of composite LiFePO_4 and carbon

Sonochemical activation

Li_3PO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and PVA

Ultrasonic processor VCX 750

Ultrasound frequency 20 kHz

Amplitude 80%, pulse on 2s, pulse off 1s

$T = 600^\circ\text{C}$, $t = 1.5 \text{ h}$ in Ar/H_2 (95 : 5)





Synthesis of composite LiFePO_4 and carbon

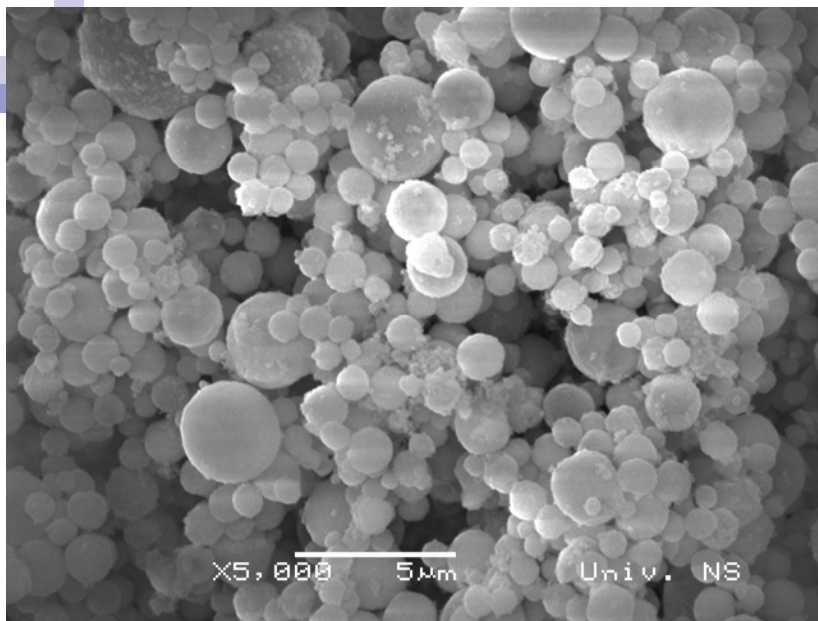
Precipitation in molten stearic acid

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, LiNO_3 , and stearic acid molar ratio

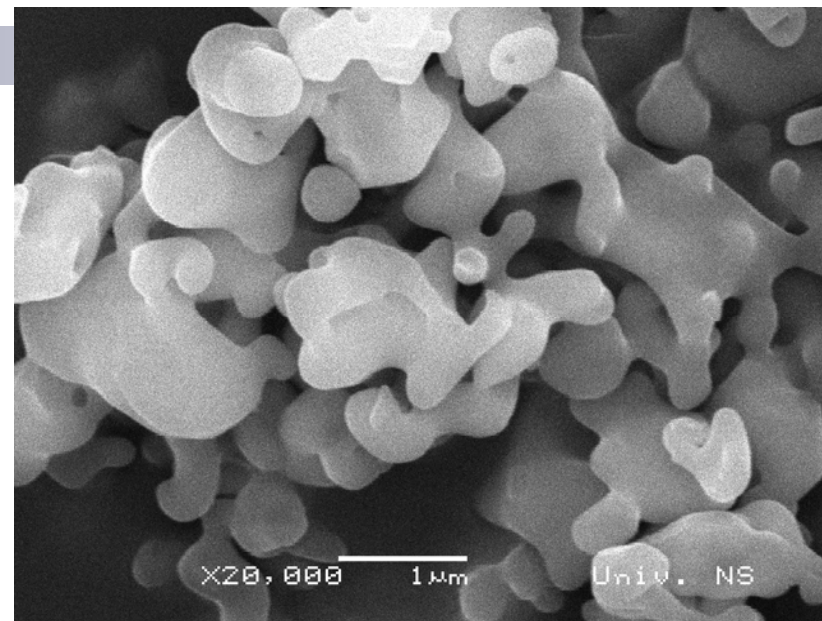
$\text{Fe} : \text{Li} : \text{P} : \text{stearic acid} = 1 : 1 : 1 : 1$

$T = 600, 700, \text{ and } 800 \text{ }^\circ\text{C}$ in argon for 3 hours

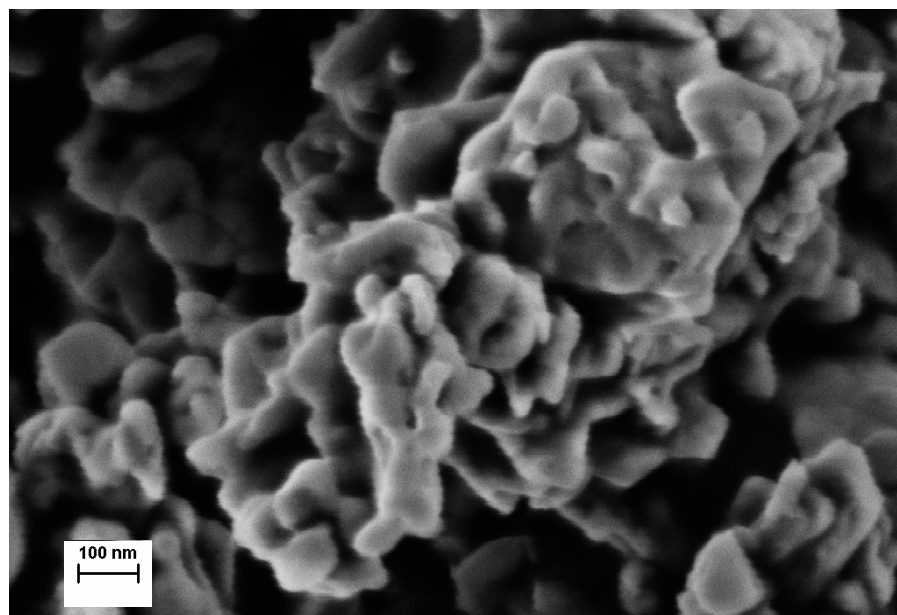
As a dispersant and a surfactant stearic acid is cheap, environmentally friendly, and provides a stable environment for moisture sensitive precursors because of its hydrophobic nature. During pyrolytic degradation in inert atmosphere stearic acid decomposes in several steps that include decarboxylation, cracking and finally decomposition to carbon while creating reductive atmosphere mostly made of liquid and gaseous hydrocarbons. The in situ formed carbon should impede particle growth and suppress agglomeration.



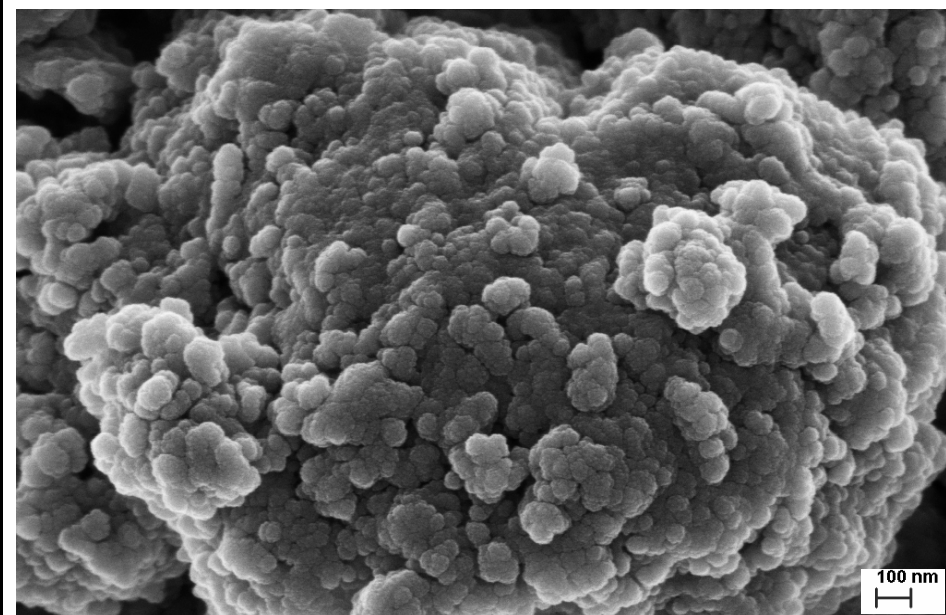
SEM image of LiFePO_4 obtained by ultrasonic spray pyrolysis. Particle size 0.8 - 3 μm .



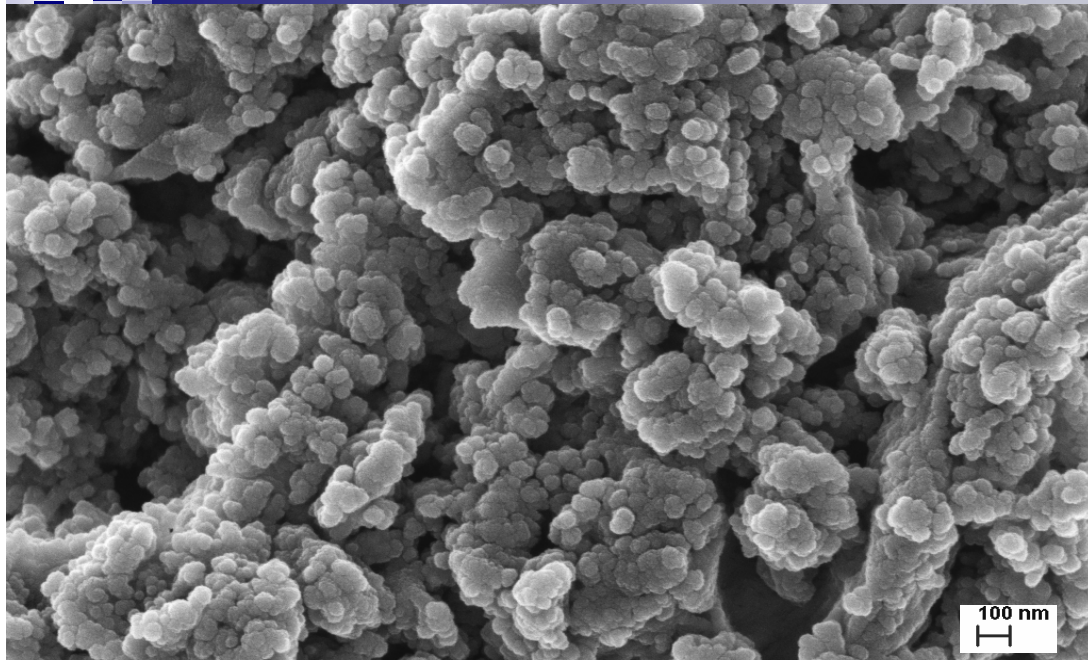
SEM image of LiFePO_4 obtained by solid state reaction. Particle size 1-2 μm .



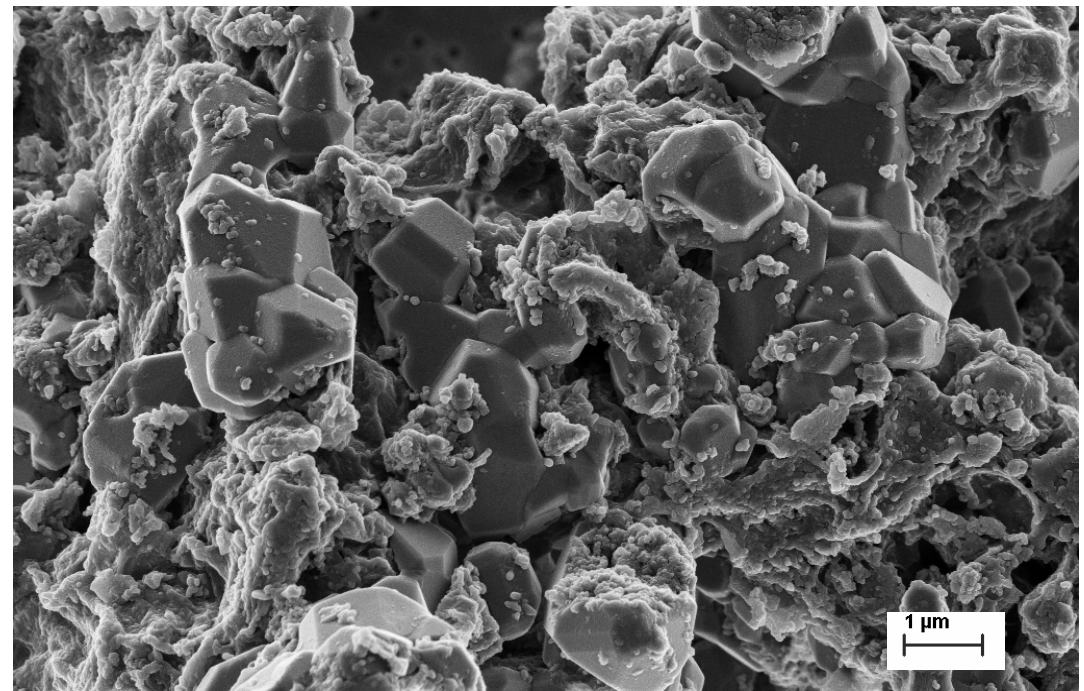
FESEM image of composite LiFePO_4/C obtained by sonochemical activation. Particle size 200- 300 nm.



FESEM image of composite LiFePO_4/C obtained by precipitation in molten stearic acid. Nodular structure. $T=700^\circ\text{C}$

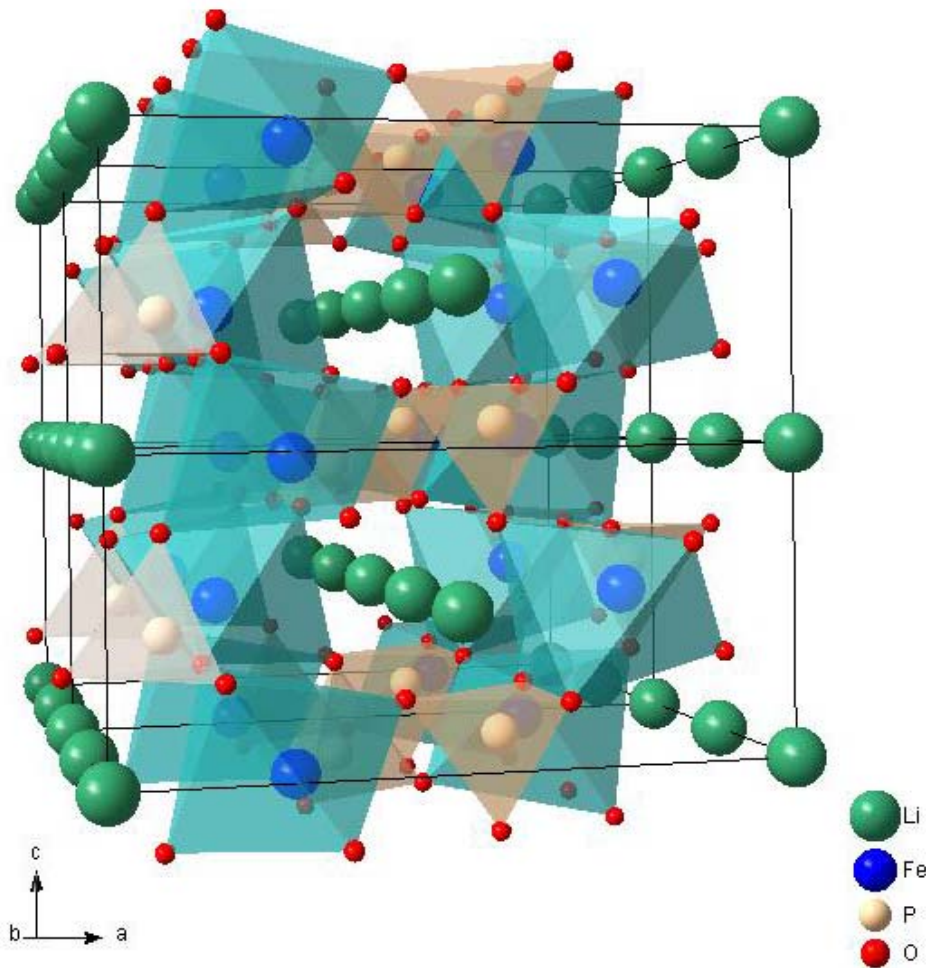


FESEM image of composite LiFePO_4/C obtained by precipitation in molten stearic acid. $T = 600\text{ }^\circ\text{C}$



FESEM image of composite LiFePO_4/C obtained by precipitation in molten stearic acid. $T = 800\text{ }^\circ\text{C}$

The structure of LiFePO_4



The olivine structure that typifies LiFePO_4 has a slightly distorted hexagonal close-packed oxygen array where Fe ion occupies octahedral site (M2), Li occupies octahedral site (M1), and P occupies tetrahedral site.

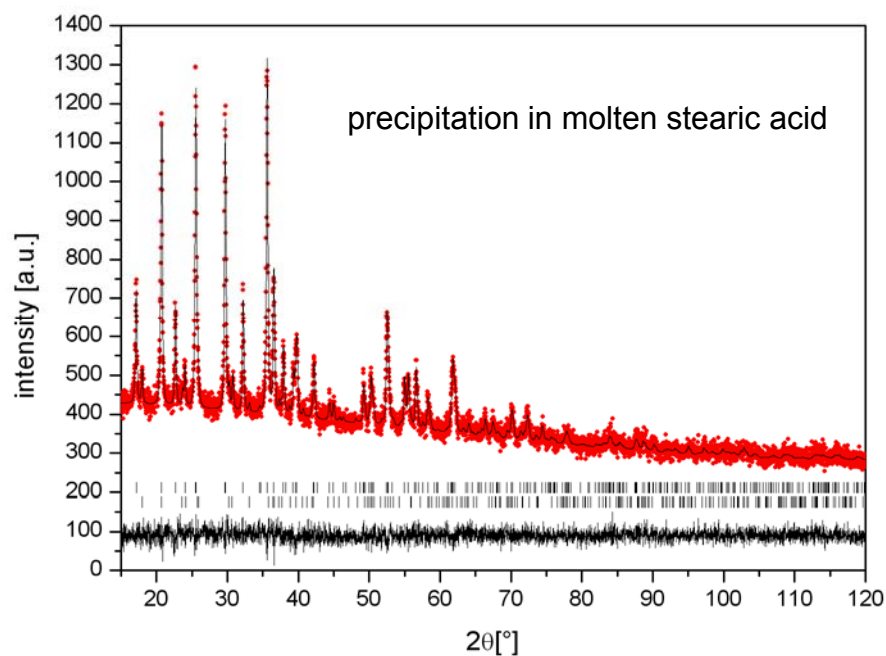
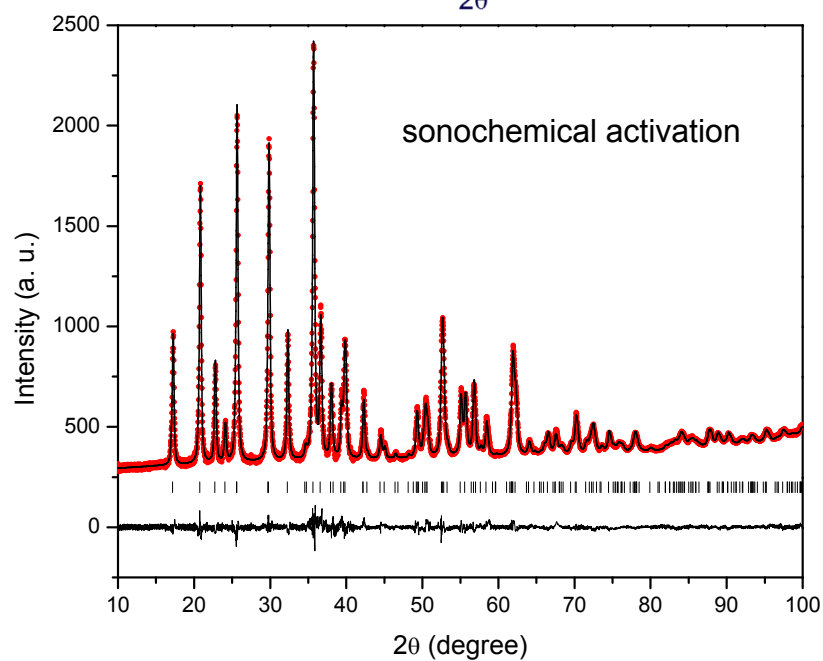
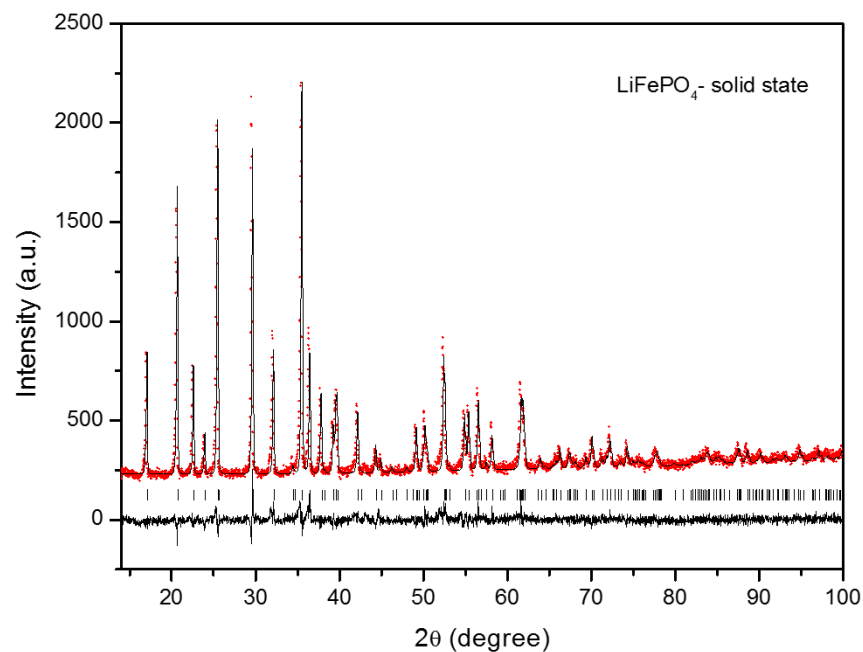
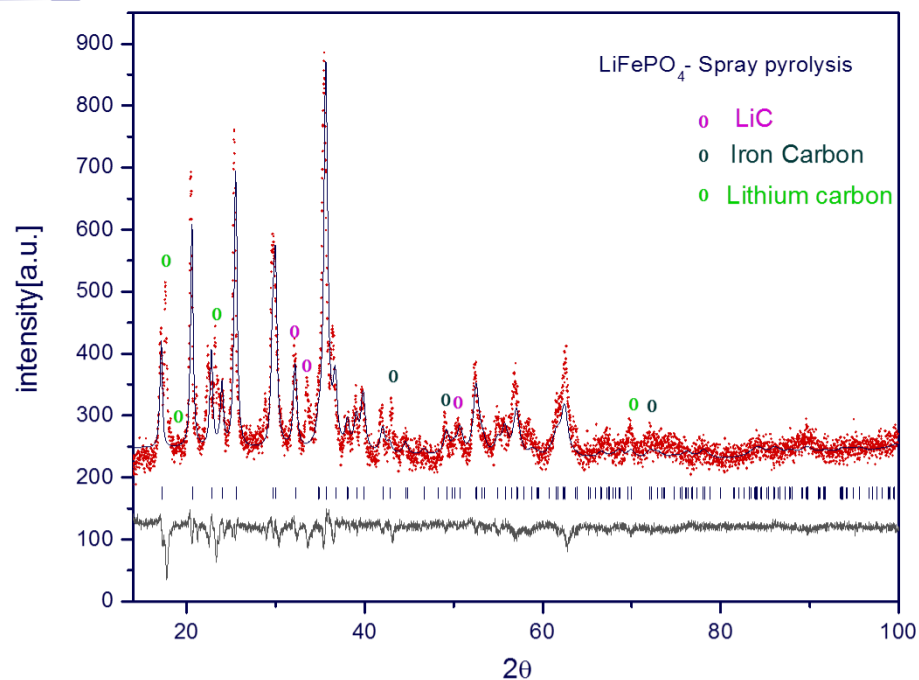
There is no continuous network of FeO_6 edge-shared octahedra that might contribute to electronic conductivity; instead, the divalent Fe ions occupy corner-shared octahedra. Therefore, the main obstacles in reaching theoretical capacity are its low electronic and low ionic conductivity.

Li/Fe “anti-site” disorder is intrinsic property (1-2 mol%).

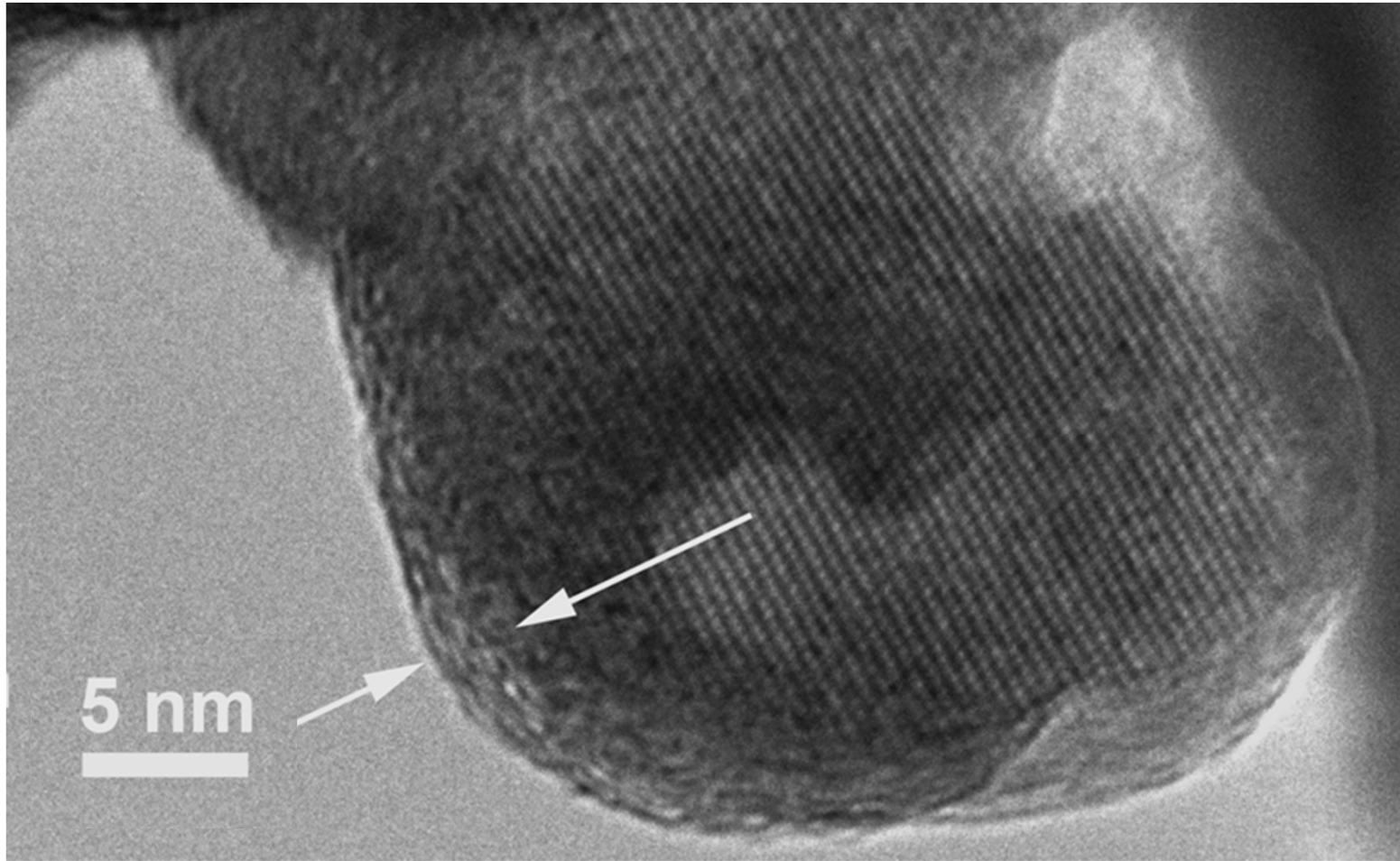
Li motion through crystal structure occurs along the one-dimensional channel along the b axis, which can become blocked by ionic disorder, by foreign phases, or by stacking faults.

When lithium ion is extracted from LiFePO_4 host the formed phase is isostructural FePO_4 (heterosite).

Rietveld refinements of XRPD data



TEM images of composite LiFePO_4/C obtained by sonochemical activation

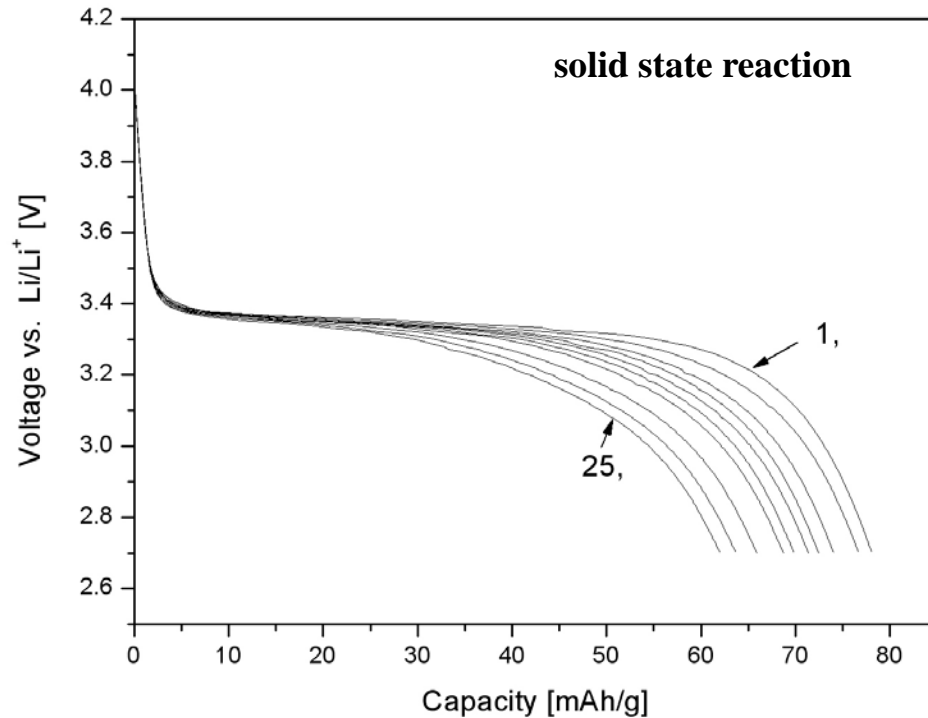


On the thin particle edges carbon film with a typical thickness of several nanometers can be observed.

The main results of Rietveld refinement

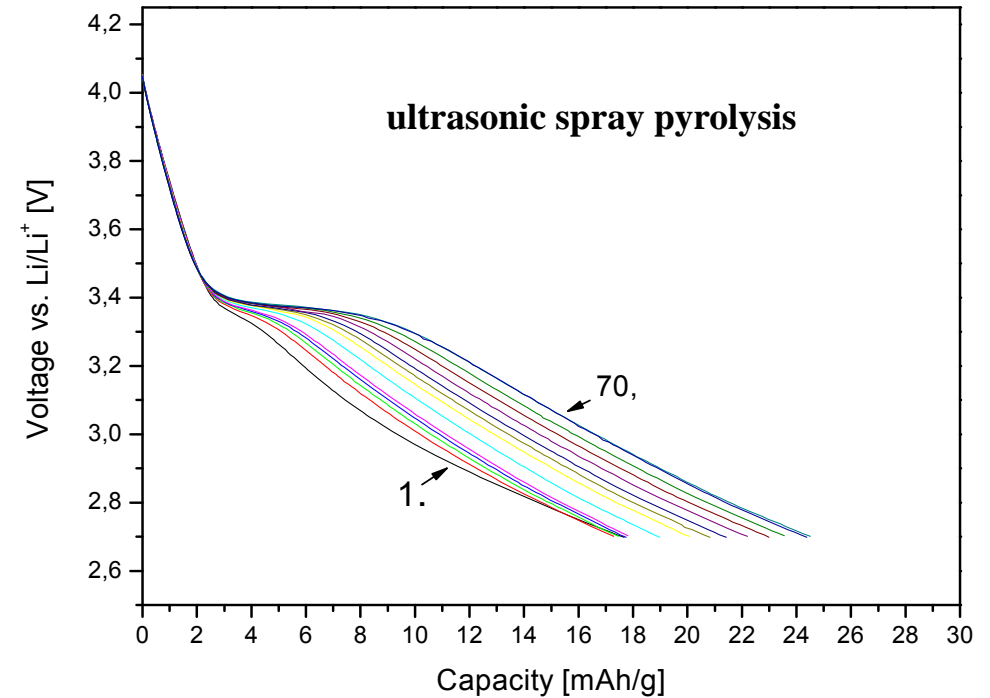
Sample	LFP_SS	LFP_SP	LFP_SA	LFP_PSA (700)	
Lattice parameters [Å]	a = 10.3299(3) b = 6.0053(2) c = 4.6932(2)	a = 10.281(9) b = 5.946(5) c = 4.725(4)	a = 10.3149(6) b = 5.9984(4) c = 4.7010(3)	LiFePO ₄ (89%) a = 10.3279(3) b = 6.0096(2) c = 4.6994(1)	FePO ₄ (11%) a = 9.8439(4) b = 5.8089(2) c = 4.7809(2)
Primitive cell volume [Å ³]	291.14(2)	288.9(4)	290.86(3)	291.68(9)	273.38(9)
Mean crystallite size [nm]	600(20)	190(15)	70(5)	75(4)	
Microstrain [%]	0.070(9)	1.2(1)	0.23(2)	0	
Li site occ. by Fe			0.03(4)	0.02(5)	
R factor [%]	Rwp = 5.3	Rwp = 8.1	Rwp = 2.3	Rwp = 3.7	

Electrochemical performances



Low electrochemical activity due to transport limitations (50 % of theoretical capacity):

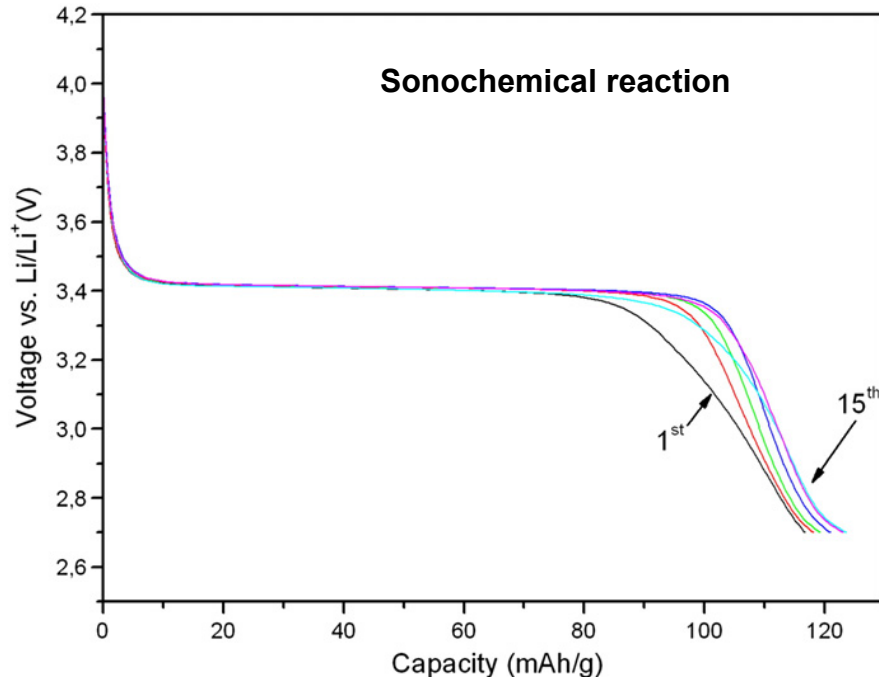
- large particles
- no carbon coating



Very low electrochemical activity (14 % of theoretical capacity):

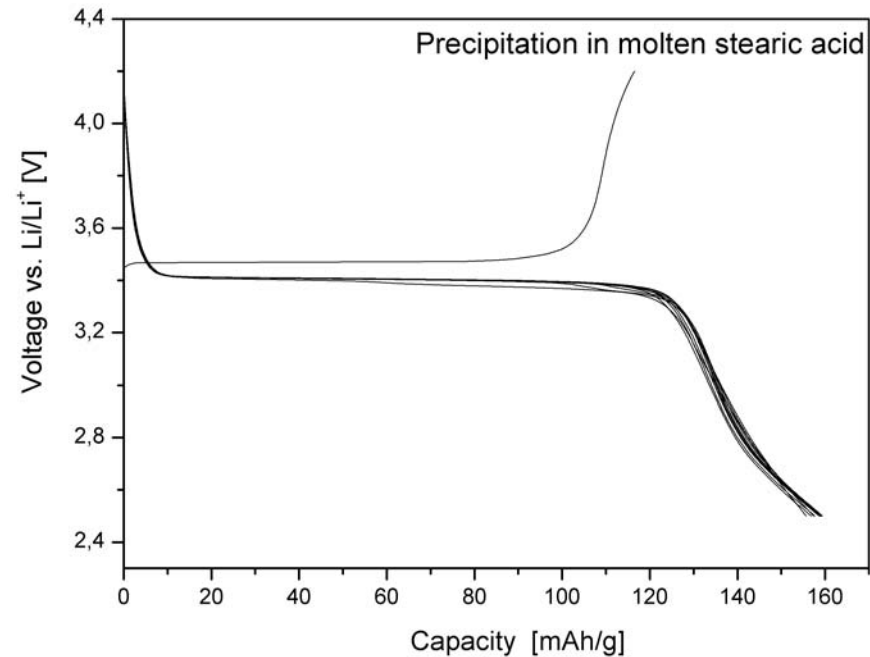
- Imperfect structure due to fast crystallization
- Presence of impurity phases

Electrochemical performances



Good electrochemical performances (73 % of theoretical capacity):

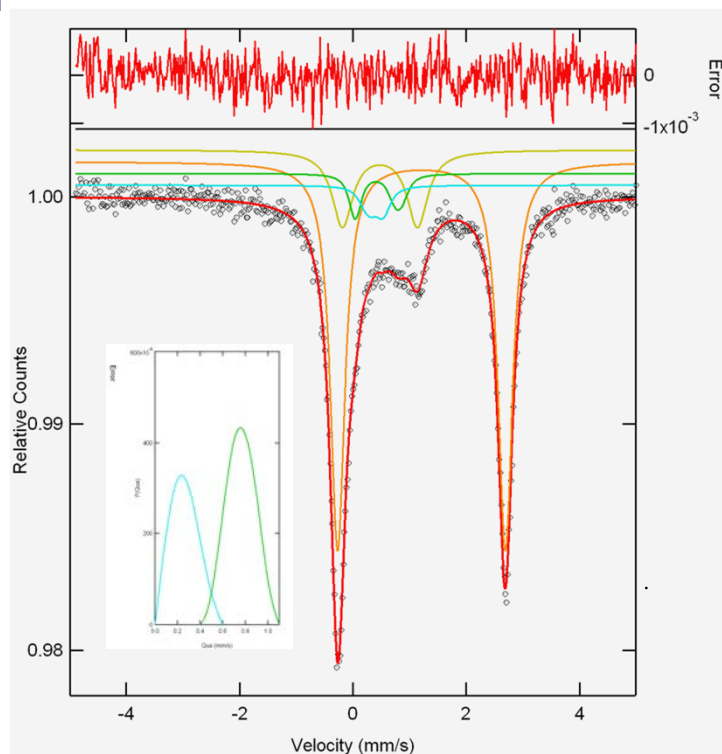
- Small particles
- Carbon coated powders
- Material fails to be fully utilized probably because of Li/Fe antsite disorder



Very good electrochemical performances (95 % of theoretical capacity):

- Small particles
- Carbon coated powders
- Small value of Li/Fe antsite disorder
- Significant difference in capacity for the first charge/discharge processes.

Mössbauer spectrum of LiFePO₄/C obtained by precipitation



Mössbauer spectroscopy implied the presence of octahedrally coordinated Fe²⁺ and Fe³⁺ ions, which can be assigned to olivine LiFePO₄ and heterosite FePO₄, respectively, and also the presence of tetrahedrally coordinated Fe³⁺ ions with distribution of quadrupolar effects indicating nanoparticulate or amorphous nature of that phase.

The first charge capacity is proportional to the amount of Fe²⁺ ions present in powder calculated by Mössbauer spectroscopy. Heterosite also FePO₄ participated in electrochemical reactions.

<i>Site</i>	<i>Area [%]</i>	<i>δ [mm/s]</i>	<i>Δ [mm/s]</i>	<i>Γ [mm/s]</i>
Fe ²⁺ (O _h)	70(1)	1.210(1)	2.959(3)	0.311(4)
Fe ³⁺ (O _h)	19(2)	0.48(1)	1.32(3)	0.44(3)
<i>Distributions:</i>		<i>< δ ></i>	<i>< Δ ></i>	<i>SD</i>
Fe ³⁺	4.5	0.40(7)	0.264	0.116
Fe ³⁺	6.5	0.42(7)	0.759	0.126

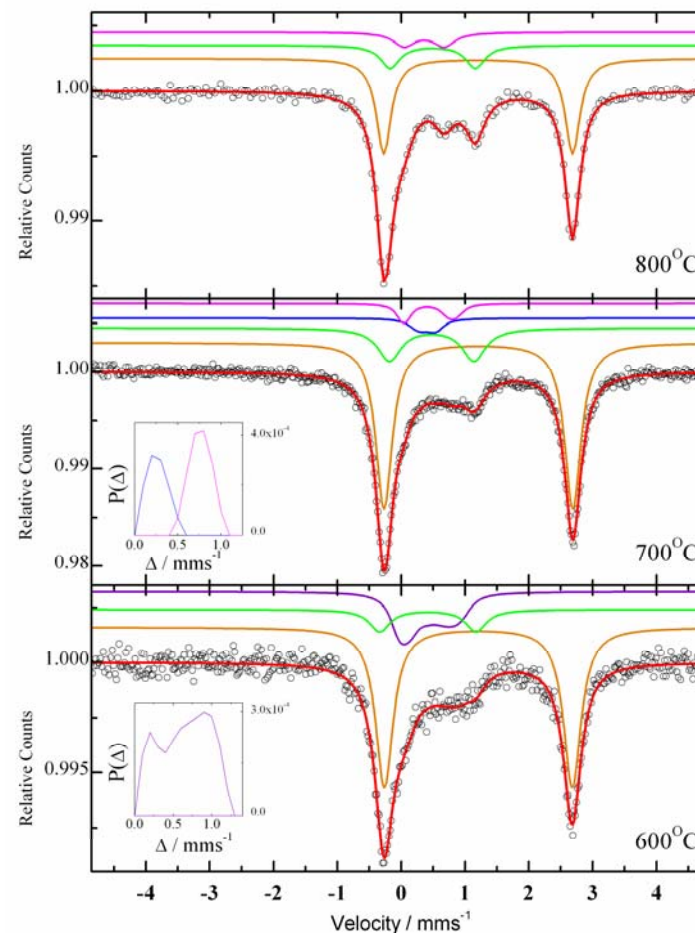
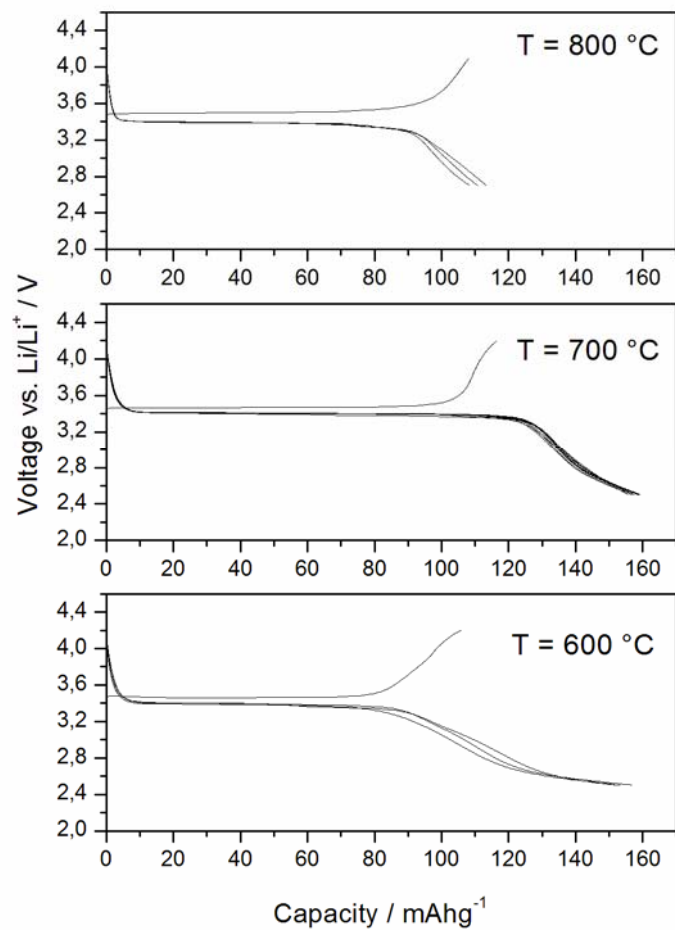
Mössbauer parameters:

δ - isomer shift

Δ - quadrupole splitting

Γ - full width with half maximum

Precipitation in molten stearic acid





CONCLUSION

Different synthesis routes of olivine type LiFePO_4 lead to different morphologies, structural, microstructural, and transport properties. The powder with optimal electrochemical performances was obtained by using aqueous precipitation in molten stearic acid; simple, scaleable, “green”, and inexpensive method.

Well crystallized, small particles without structural imperfections, and coated with carbon are important demands for obtaining excellent electrochemical performances.

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These researches present the joint work of several institutions

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