

## Supplementary information : Insertion of fluorine in LiFePO<sub>4</sub> electrode material by gas-solid fluorination

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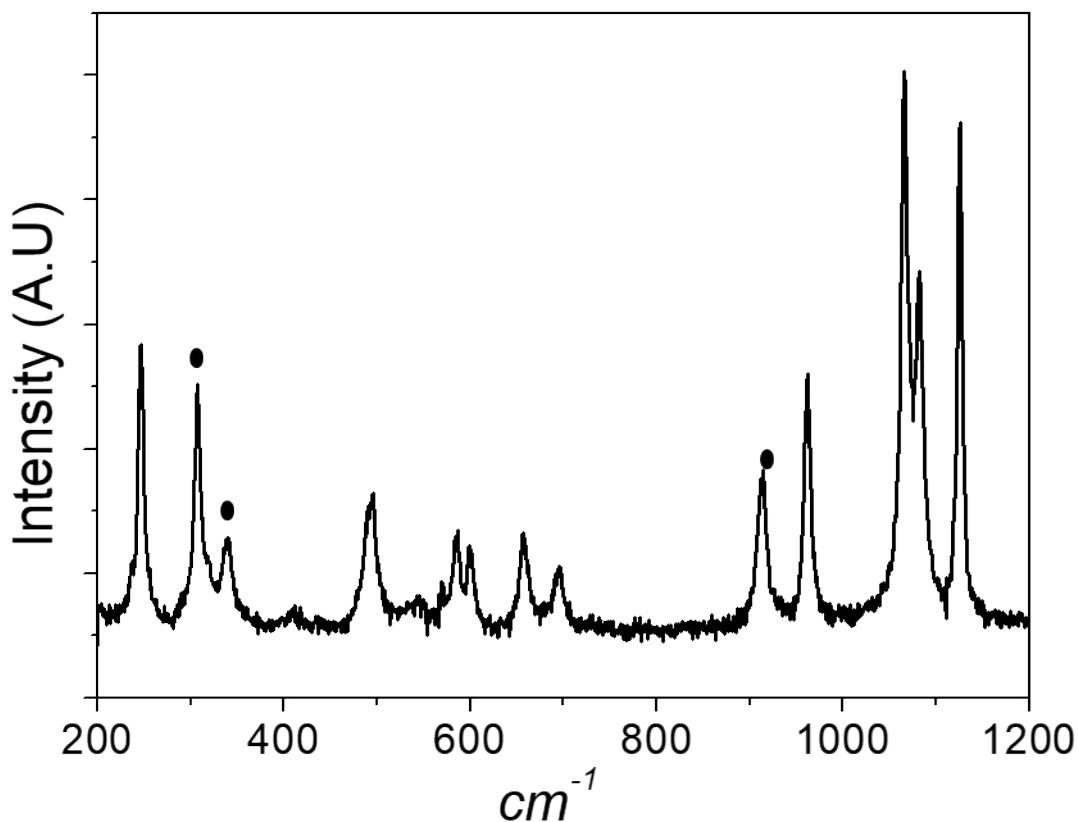


Figure S1 : Raman spectra of LiFePO<sub>4</sub> fluorinated at 125°C, black dots corresponding to FePO<sub>4</sub>.

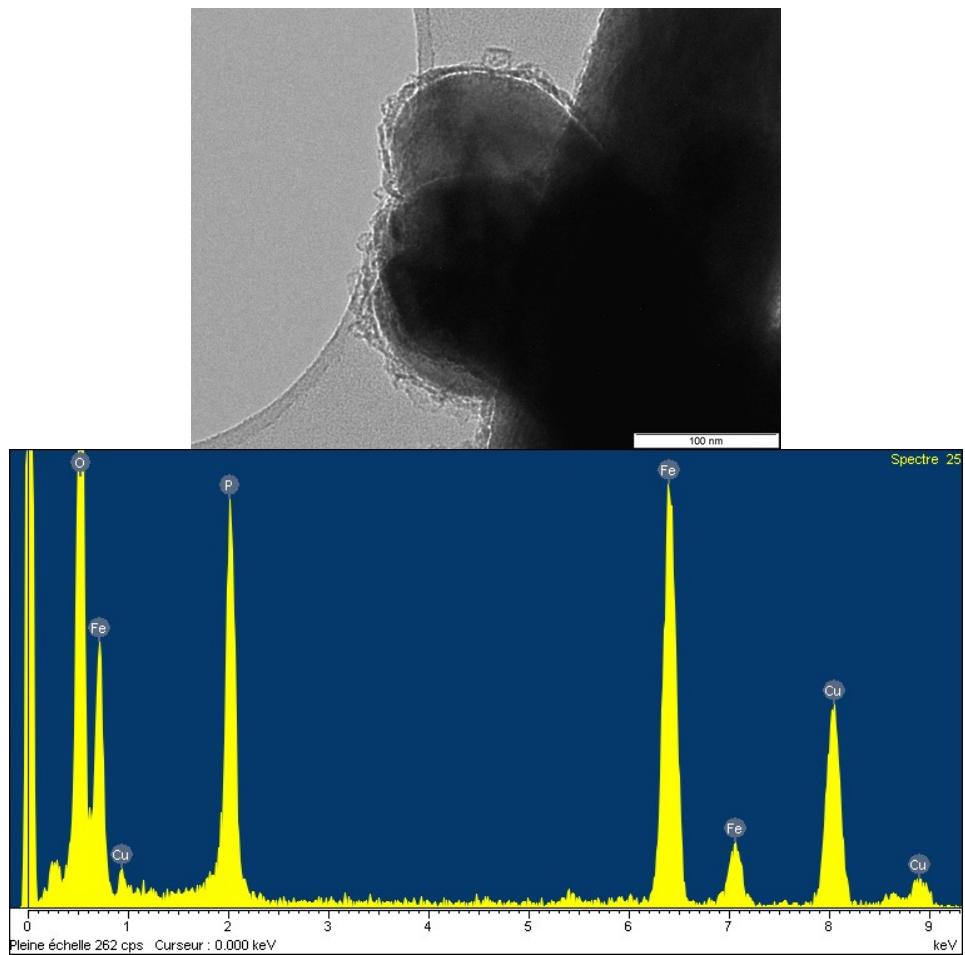


Figure S2 : Transmission electronic microscopy image (TEM) and chemical analysis by Energy Dispersive Spectrometry (TEM-EDS) of  $\text{LiFePO}_4 + \text{F}_2$  125°C particles core.

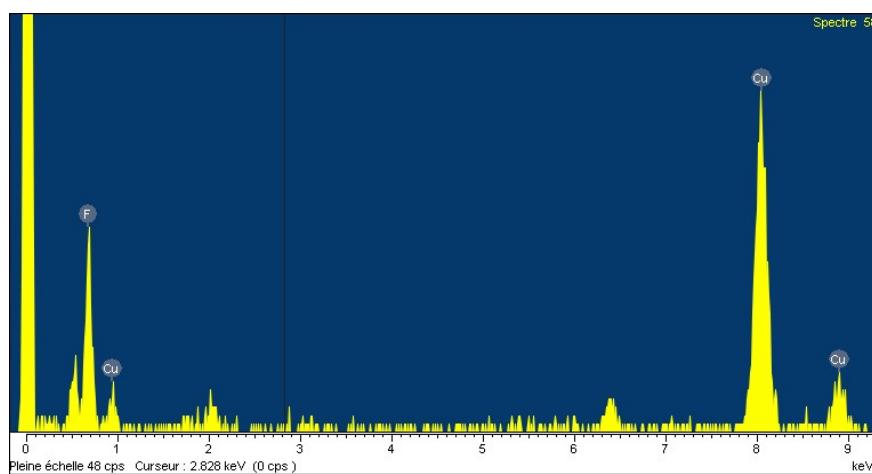
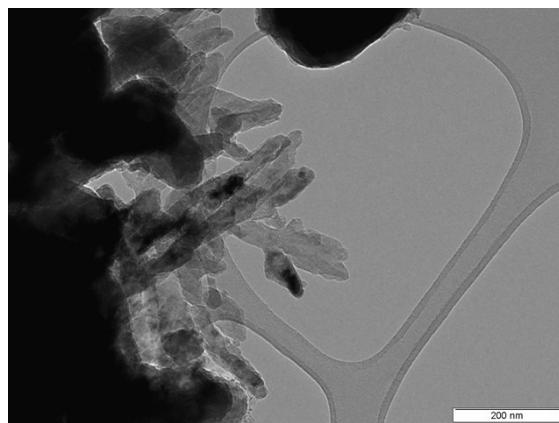


Figure S3 : Transmission electronic microscopy (TEM) and chemical analysis by Energy Dispersive Spectrometry (TEM-EDS) of LiFePO<sub>4</sub> + F<sub>2</sub> 125°C particles shell.

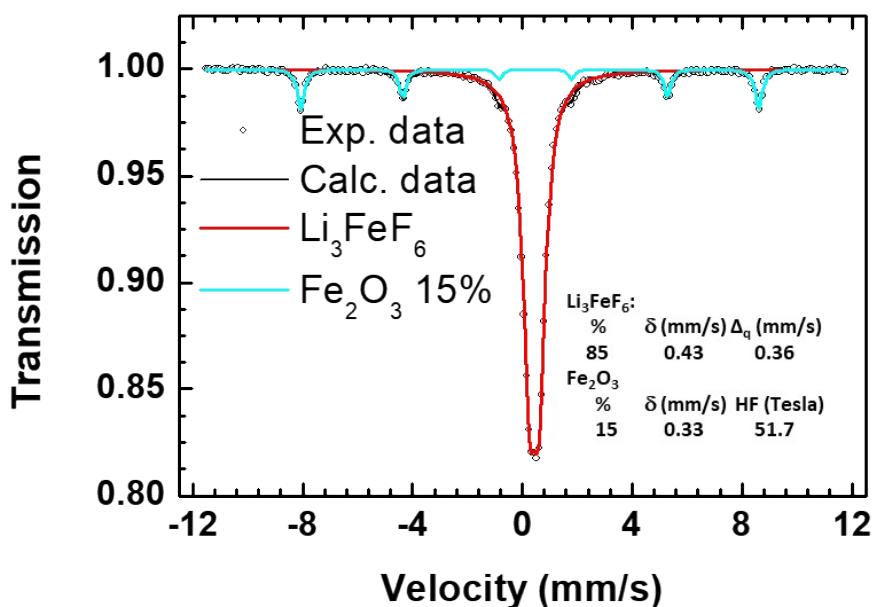


Figure S4 : <sup>57</sup>Fe Mössbauer spectra at 300 K of α-Li<sub>3</sub>FeF<sub>6</sub> obtained with Li<sub>2</sub>CO<sub>3</sub> + FePO<sub>4</sub>.4H<sub>2</sub>O in Hf<sub>aq</sub> 48% with a second treatment under F<sub>2</sub> at 250°C. Fe<sub>2</sub>O<sub>3</sub> is obtained as an impurity at 15 %Fe at.

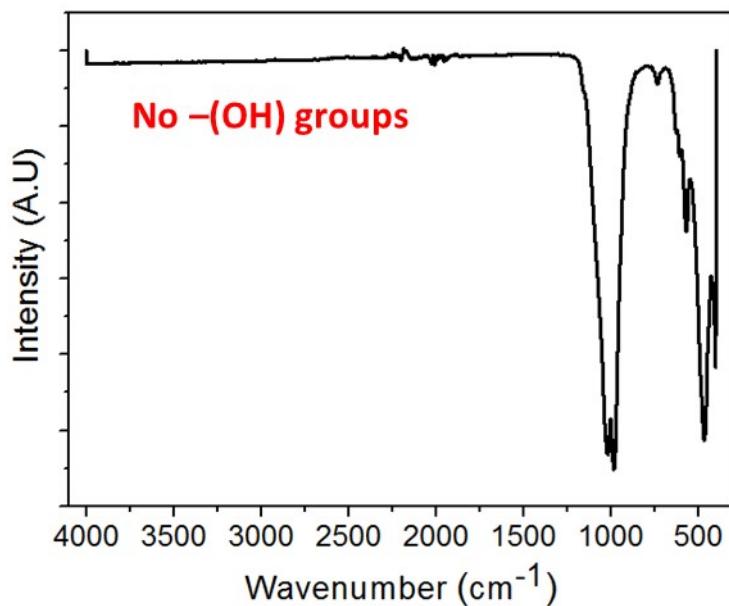


Figure S5 : IR spectra of  $\text{LiFePO}_4 + \text{F}_2$  125°C –  $\text{N}_2$ .

Table S1: Synthesis conditions for the obtention of the different fluorinated materials

| Coumpound              | Treatment                                  | Label                                 |                  |
|------------------------|--|---------------------------------------|------------------|
| $\text{LiFePO}_4$      | -  | $\text{LiFePO}_4$                     | Pristine         |
|                        | $\text{F}_2$ at RT                         | $\text{LiFePO}_4 + \text{F}_2$ - RT   |                  |
|                        | $\text{F}_2$ at 125°C                      | $\text{LiFePO}_4 + \text{F}_2$ - 125  | Low Temperature  |
|                        | $\text{F}_2$ at 250°C                      | $\text{LiFePO}_4 + \text{F}_2$ - 250  |                  |
|                        | $\text{F}_2$ at 350°C                      | $\text{LiFePO}_4 + \text{F}_2$ - 350  |                  |
|                        | $\text{F}_2$ at 500°C                      | $\text{LiFePO}_4 + \text{F}_2$ - 500  | High Temperature |
| $\text{LiFePO}_4$ -RT  | annealing under $\text{N}_2$ (550°C ; 24h) | $\text{LiFePO}_4$ - RT + $\text{N}_2$ | Annealed         |
| $\text{LiFePO}_4$ -125 | annealing under $\text{N}_2$ (550°C ; 24h) | $\text{LiFePO}_4$ -125 + $\text{N}_2$ | Annealed         |