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Investigating LiFePO₄ electrode degradation in water-in-salt electrolyte

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Lithium-ion battery safety can be enhanced by replacing the flammable organic-electrolyte by a water based one. Unfortunately, the electrochemical stability window of water is limited (1.23 V) but can be enhanced with water-in-salt electrolyte (WISE) where the salt exceeds the solvent in mass and volume. High salt concentration reduces drastically water molecule activity, pushing further Hydrogen Evolution Reaction (HER) and Oxygen Evolution Reaction (OER) potential, broadening the electrolyte electrochemical stability window up to 3 V¹. However, during cycling, several issues linked to the release of free water molecules occur leading to poor electrochemical performance.

In the present case, we decided, to investigate the impact of WISE on LiFePO₄ positive electrode materials prior cycling. The question being if the decompositions are driven by the electrochemical response or if the surface chemistry can play a role even before starting cycling. To do so, LiFePO₄ electrodes were soaked during 24 h in aqueous electrolyte at different salt concentration (from 0 mol·kg⁻¹ to 21 mol·kg⁻¹), then washed and dried before being investigated with multi-scale characterisation techniques. First, the soaked electrodes were cycled using Galvanostatic Cycling with Potential Limitation (GCPL) to evaluate the impact of the soaking on the electrochemical performance in classic organic-based electrolyte (Figure 1). As can be seen, soaking the electrode in water is detrimental since the specific charge is lower than pristine (unsoaked) sample. In the case of the electrodes soaked in WISE, the electrochemical performance remains closely the same as the pristine but a polarisation is seeing building up maybe related to a change of surface chemistry.

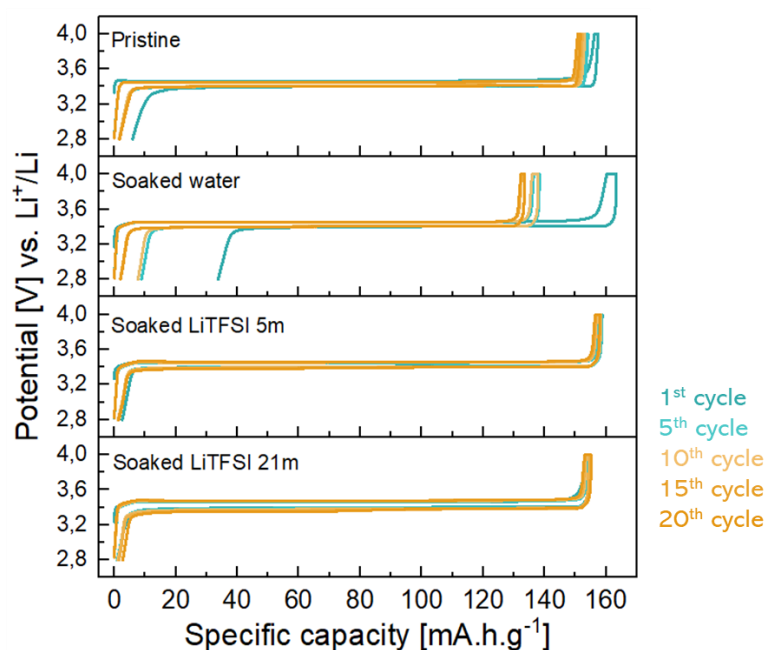


Figure 1 – Specific capacity of LiFePO₄ soaked electrode obtained in coin cell vs Li metal at C/20 rate.

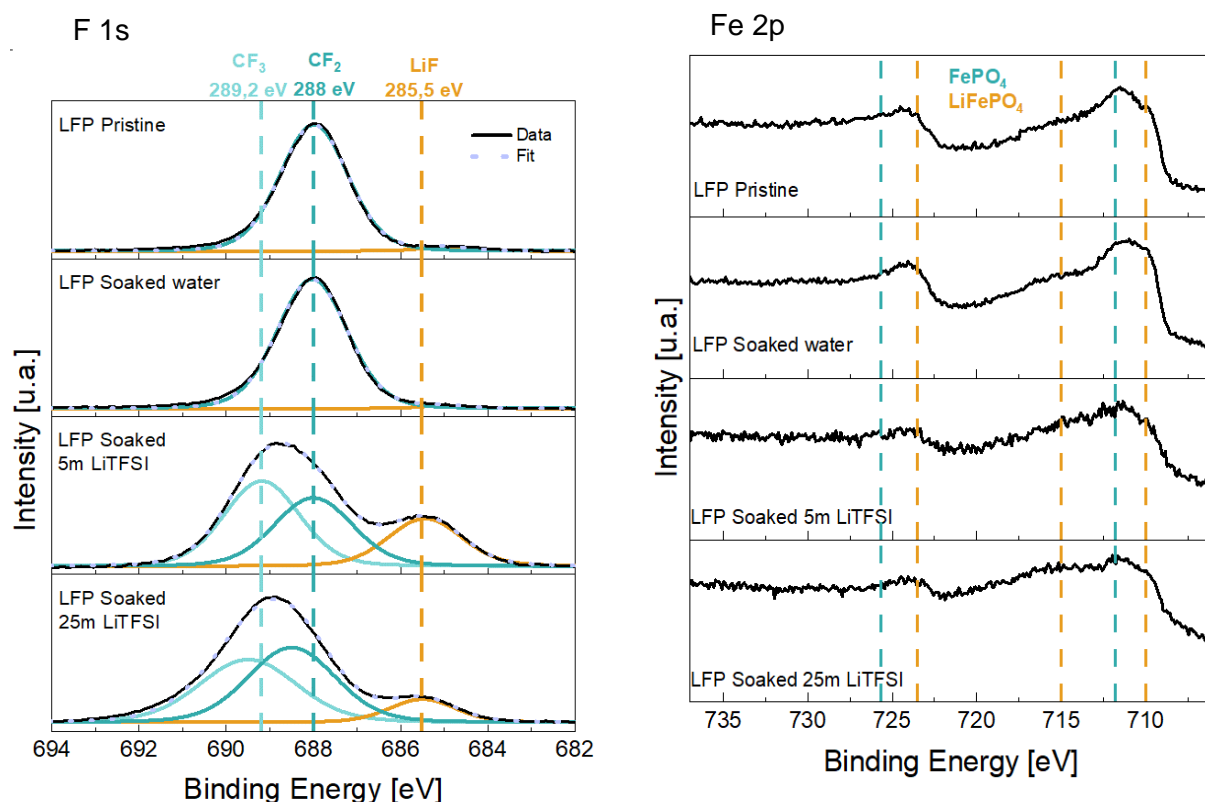


Figure 2 – F 1s and Fe 2p XPS spectra of unsoaked and soaked electrodes

Additional investigations were carried out by X-ray photoelectron spectroscopy (XPS) in order to investigate the upper surface of the electrode (~ 7 nm) to determine the surface chemistry. Moreover, X-ray absorption spectroscopy (XAS) was used to assess iron oxidation state of the electrode both at the surface, using X-ray fluorescence micro XAS (ID21 beamline at ESRF) and in the bulk, through transmission measurement (SNBL beamline at ESRF).

Results tend to indicate surface decomposition of the active material with an evolution of Fe and Li loss depending on the electrolyte salt concentration. LiF contribution on F 1s spectrum (Figure 2) recalls the formation of a protective layer on the electrode coming from the decomposition products of the salt in the organic electrolytes and/or the decomposition of the binder², its formation process is yet to be understood and will be investigated in our water-in-salt system. A clear evolution of the surface species, depending on the presence of the salt in the aqueous electrolyte, demonstrates interaction between the electrode's materials and the electrolyte. XAS measurement performed in transmission at the Fe K-edge reveals mostly no modification indicating that the bulk might not be affected by the soaking process.

The correlation of the results gathered from multi-scale characterisation techniques, helps us to address the degradation mechanisms occurring in water-in-salt batteries.

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(2) Castro, L.; Dedryvère, R.; El Khalifi, M.; Lippens, P.-E.; Bréger, J.; Tessier, C.; Gonbeau, D. The Spin-Polarized Electronic Structure of LiFePO₄ and FePO₄ Evidenced by in-Lab XPS. *J. Phys. Chem. C* **2010**, *114* (41), 17995–18000. <https://doi.org/10.1021/jp106631v>.