

A DIRECT RECYCLING PROCESS OF LFP-BASED LITHIUM-ION BATTERIES TOWARDS CIRCULAR ECONOMY

Hydro-Québec has developed a unique direct recycling process to recover cathode material from spent LFP-based batteries based on a two-step process:

1. Delithiation of LFP to FP using H_2O_2 and CO_2
2. Relithiation of FP particles back to LFP using two innovative direct and indirect electrochemical approaches

For direct electrochemical approach, the FP is coated on a current collector and used as cathode in a cell containing Li_2SO_4 or $LiHCO_3$ solutions. In the case of indirect approach, the reducing agent is the reduced form of a redox couple that has a redox potential lower than the reduction potential of FP to LFP and higher than the hydrogen evolution reaction.

The new approach from Hydro-Québec allows to achieve the main three objectives of being environmentally friendly, and economically viable as well as producing a battery grade material as final product.

MAIN OBJECTIVES AND STEPS OF THE NEW DEVELOPED PROCESS

ECONOMICALLY VIABLE

Selective lixiviation of Li with very low extraction rates for Fe and P

ENVIRONMENTALLY FRIENDLY

Use of mild and preferably renewable and recyclable reagents:

CO_2

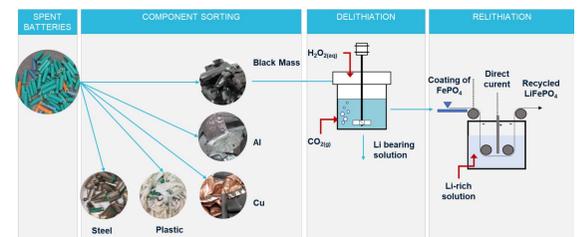
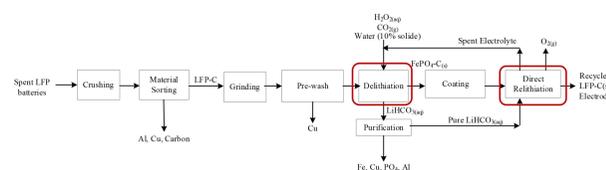
H_2O_2

Electrons as reducing agent

PRODUCES BATTERY GRADE MATERIALS AS FINAL PRODUCT

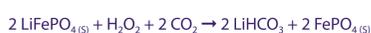
Preserving the orthorhombic structure of LFP

Preserving the carbon coating of LFP particles



LFP TO FP DELITHIATION STEP

REACTION CONDITIONS



CO2 pressure: 2 atm

Higher pressures do not increase Li solubility significantly

H2O2 : Fe ratio: between 0.6 and 1.25

Depending on solid: liquid ratio due to higher H2O2 consumption

Solid: liquid ratio: 1:100 to 1:10

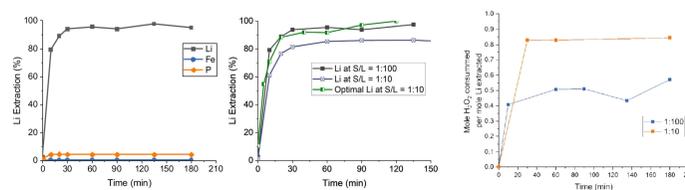
Increased solid: liquid ratio results in higher reactor productivity

Temperature: 20 – 25°C

Higher temperatures result in lower LiHCO3 solubility

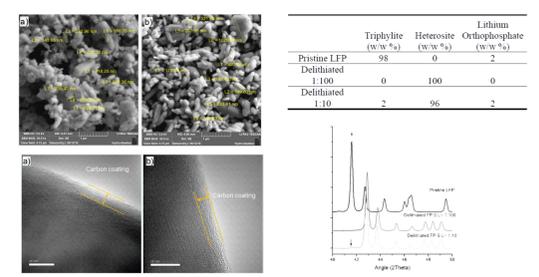
Agitation:

To promote suspension and gas dispersion



Selective delithiation at low solid: liquid ratio

Effect of solid: liquid ratio on Li extraction rate and H2O2 consumption



Effect of delithiation on morphology, carbon coating and particle structure

FP TO LFP RELITHIATION STEP

INDIRECT ELECTROCHEMICAL RELITHIATION

Chemical reactor: $FePO_4(s) + Li^+ + [Red] \rightarrow LiFePO_4(s) + [Ox]$

Electrochemical reactor:

Cathodic reaction: $2 [Ox] + 2 e^- \rightarrow 2 [Red]$

Anodic reaction: $H_2O - 2 e^- \rightarrow \frac{1}{2} O_2 + 2 H^+$

Electrochemical behaviour of EDTA/Fe complexes (CV)

Working electrode:

For LFP/FP: FP thin film coated on SS substrate

For EDTA-Fe(II)/EDTA-Fe(III): SS electrode

Counter electrode: Pt mesh

Electrolyte: 0.5 M aqueous solution of LiHCO3, pH 7

Temperature: at 25°C

Scan rate: of 200 mV s⁻¹

Observations

Onset of FP reduction at potentials lower than 0,4 V (vs NHE)

A redox couple with a lower reduction potential can be used as reducing agent

H2 evolution onset at around -0.8 V (vs NHE)

The coulombic efficiency of the direct electrochemical reduction is potentially very high

Relithiation of FP to LFP with EDTA/Fe2+ and Li2SO4

Li salt: 0.9 M aqueous solution Li2SO4, pH 8

Reducing agent: 0.1 M aqueous solution of EDTA/Fe2+

EDTA/Fe2+ : FePO4 ratio: 1.16: 1

Temperature: at 40°C

Agitation: magnetic stirrer and Ar bubbling

Reaction time: 100 min.

Electrochemical regeneration of EDTA/Fe3+

Electrochemical cell: ICI FM01 parallel plate

Cathode: graphite

Anode: DSA (Ir oxide on Ti)

Membrane: cation exchange Nafion 324

Temperature: at 40°C

Agitation: electrolyte recirculation at 16 cm/s

Initial electrolyte: Li2SO4 1M, EDTA 0.2 M and Fe3+ 0.08 M

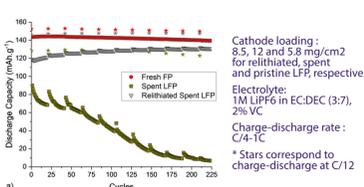
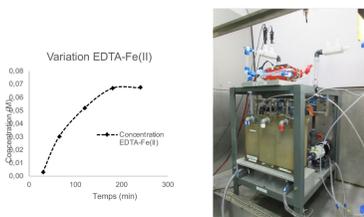
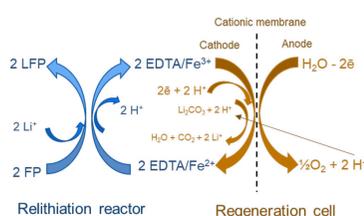
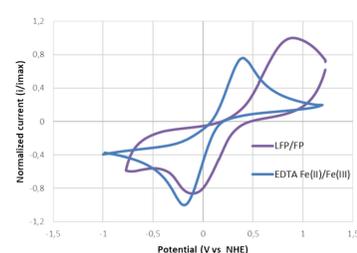
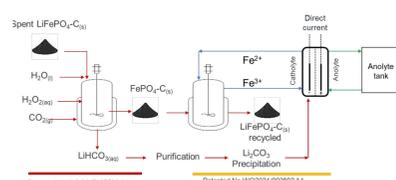
Mode: controlled voltage at 1.65 V

Electrochemical performance of relithiated spent LFP

Spent LFP presents a low starting capacity of around 90 mAh/mg and a very rapid loss in capacity at 1C

Recycled LFP shows practically same capacities at C/12 (96%) and lower initial capacity at 1C compared to fresh LFP (83%)

After 210 cycles, delithiated and relithiated LFP shows 98% capacity at C/12 and 94% at 1C compared to fresh LFP



DIRECT ELECTROCHEMICAL RELITHIATION

Cathodic reaction: $2 FePO_4(s) + 2 Li^+ + 2 e^- \rightarrow 2 LiFePO_4(s)$

Anodic reaction: $2 HCO_3^- - 2 e^- \rightarrow 2 LiFePO_4 + \frac{1}{2} O_2 + H_2O$

Linear scanning voltammetry

Working electrode: FP thin film coated on SS substrate

Counter electrode: Pt mesh

Reference electrode: Ag/AgCl

Electrolyte: 0.5 M aqueous solution of LiHCO3, pH 7

Temperature: at 25°C

Scan rate: of 1 mV s⁻¹

Chronopotentiometric evaluation

Working electrode: FP thin film coated on SS substrate

Counter electrode: Pt mesh

Electrolyte: 0.5 M aqueous solution of LiHCO3, pH 7

Temperature: at 25°C

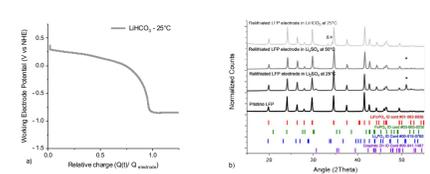
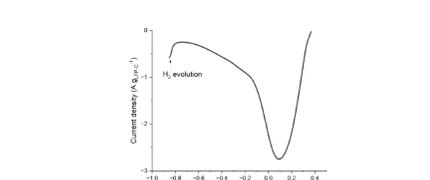
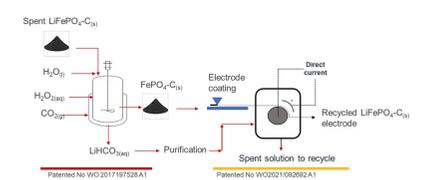
Current density: 2.4 mA/cm²

Observations

Beyond 80% relithiation, the electrode polarization starts to accelerate

H2 evolution starts after 100% relithiation

XRD analysis of the relithiated FP confirms its total conversion to LFP



CONCLUSIONS

The delithiation approach using environmentally friendly reagents (CO_2 and H_2O_2) allows for a very selective extraction of Li without any detectable alteration to the FP nanoparticles in terms of morphology and particle size as well as the carbon coating.

Direct electrochemical relithiation of the FP nanoparticles was achieved using LiHCO3 solution originated from the delithiation step. The relithiation carried out both at controlled current as well as controlled potential allowed to obtain complete relithiation to LFP and at very high current efficiencies (avoiding H2 evolution reaction).

Indirect electrochemical relithiation using EDTA/Fe2+ - EDTA/Fe3+ redox couple was shown to be very effective. Delithiated LFP was relithiated using an EDTA/Fe2+ solution and the spent solution containing EDTA/Fe3+ was regenerated back to EDTA/Fe2+ using a parallel plate electrochemical cell.

The LFP originated from the delithiation and relithiation of pristine LFP shows similar electrochemical performances as those of original pristine LFP. The LFP originated from the delithiation and relithiation of spent LFP shows more than 90% capacity of that of pristine LFP at 1C after more than 200 cycles.

