Lithium selective recovery with Electrochemical Ion Pumping for Li-ion batteries recycling

Corentin Bourdiol

Thesis director : Sylvain Franger *(Univ. Paris Saclay - ICMMO)*

Supervisors : Emmanuel Billy *(CEA - LITEN)*

Adrien Boulineau *(CEA - LITEN)*

Charly Lemoine *(CEA - LITEN)*

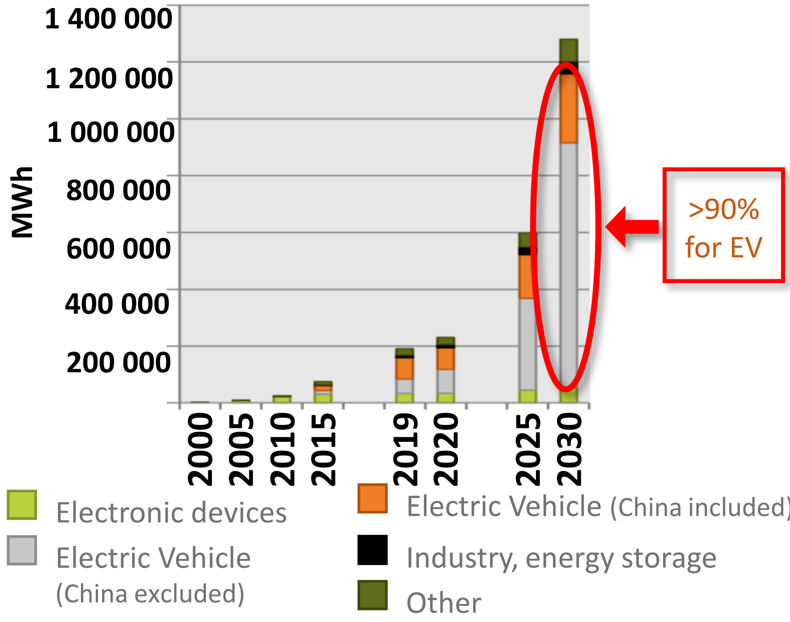
Study Context

2030 : 350 millions electric vehicle will have been produced

High increase of the worldwide Electric Vehicle (EV) market

Soon, explosion of :
end of life battery + raw material demand

Worldwide Battery Sales Forecasts (MWh) by Sector



Necessity to develop recycling processes, especially for lithium recovery

European legislation impose recycling on manufacturers

Environmental, economical and geopolitical concerns

Limited production and reserve (Li, Ni, Co, etc)

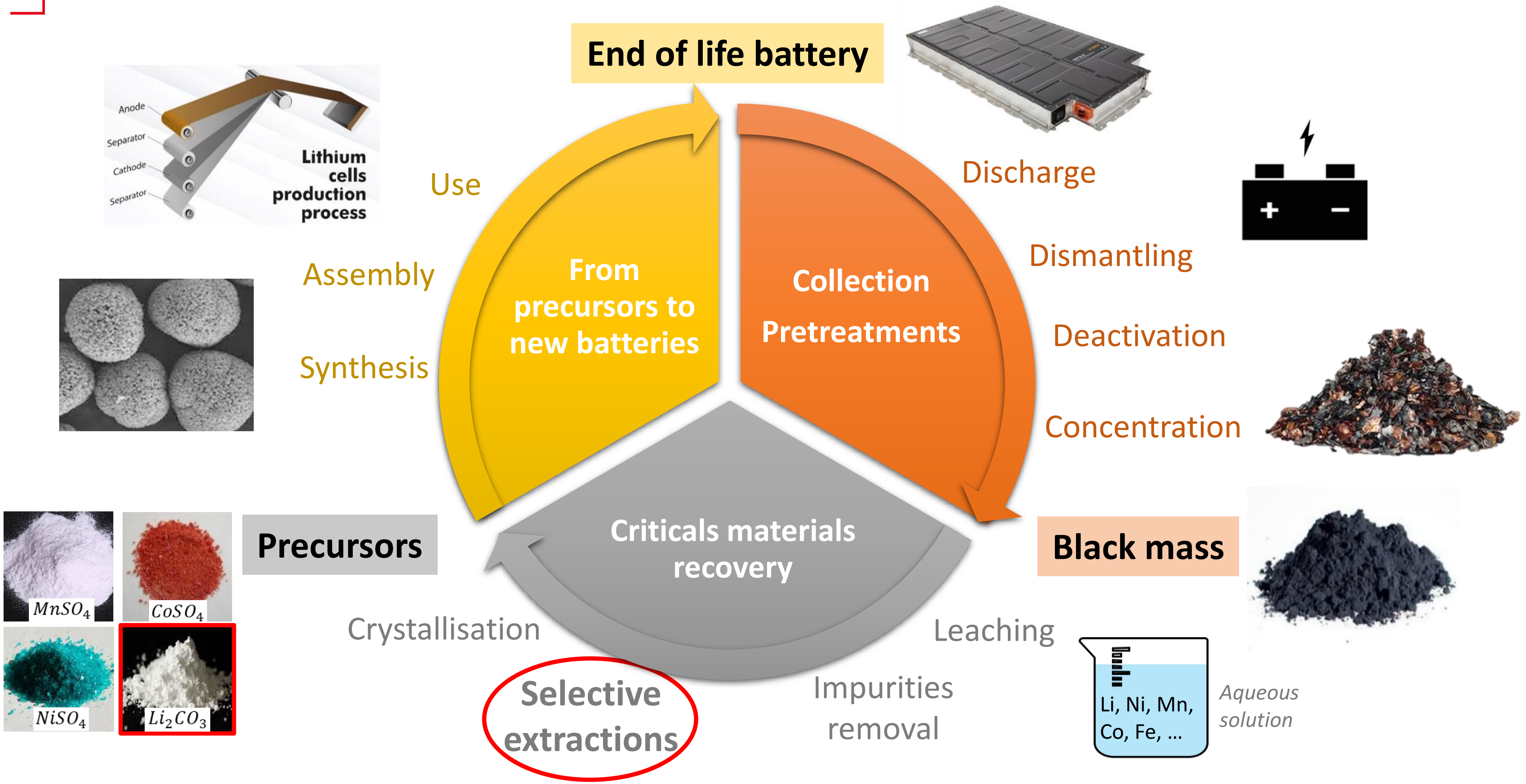
Position of the European Parliament of 14 June 2023 on EV recycling

	Recycling efficiency (%w)	Material recovery rate			
		Co	Ni	Cu	Li
Target 2027	**65%**	90%	90%	90%	**50%**
Target 2031	**70%**	95%	95%	95%	**80%**

Li is now considered as a critical material

Avicenne Energy, 2021
International Energy Agency, 2022
repealing Directive 2006/66/EC: Position of the European Parliament of 14 June 2023

State of the art: battery recycling process

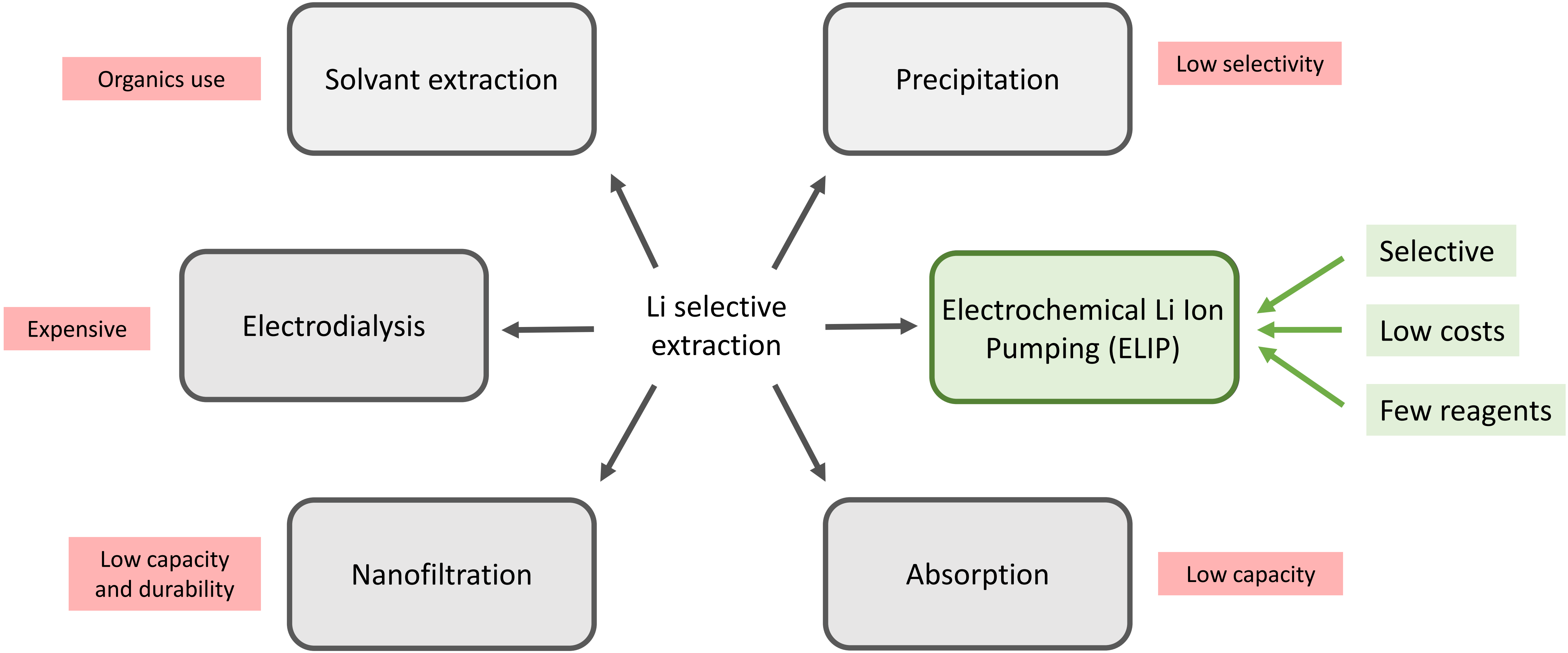


Goal : Develop a lithium selective extraction process

Recycling specificities : Complex solutions + Battery grades required

State of the art: Li extraction process

Main methods of lithium recovery



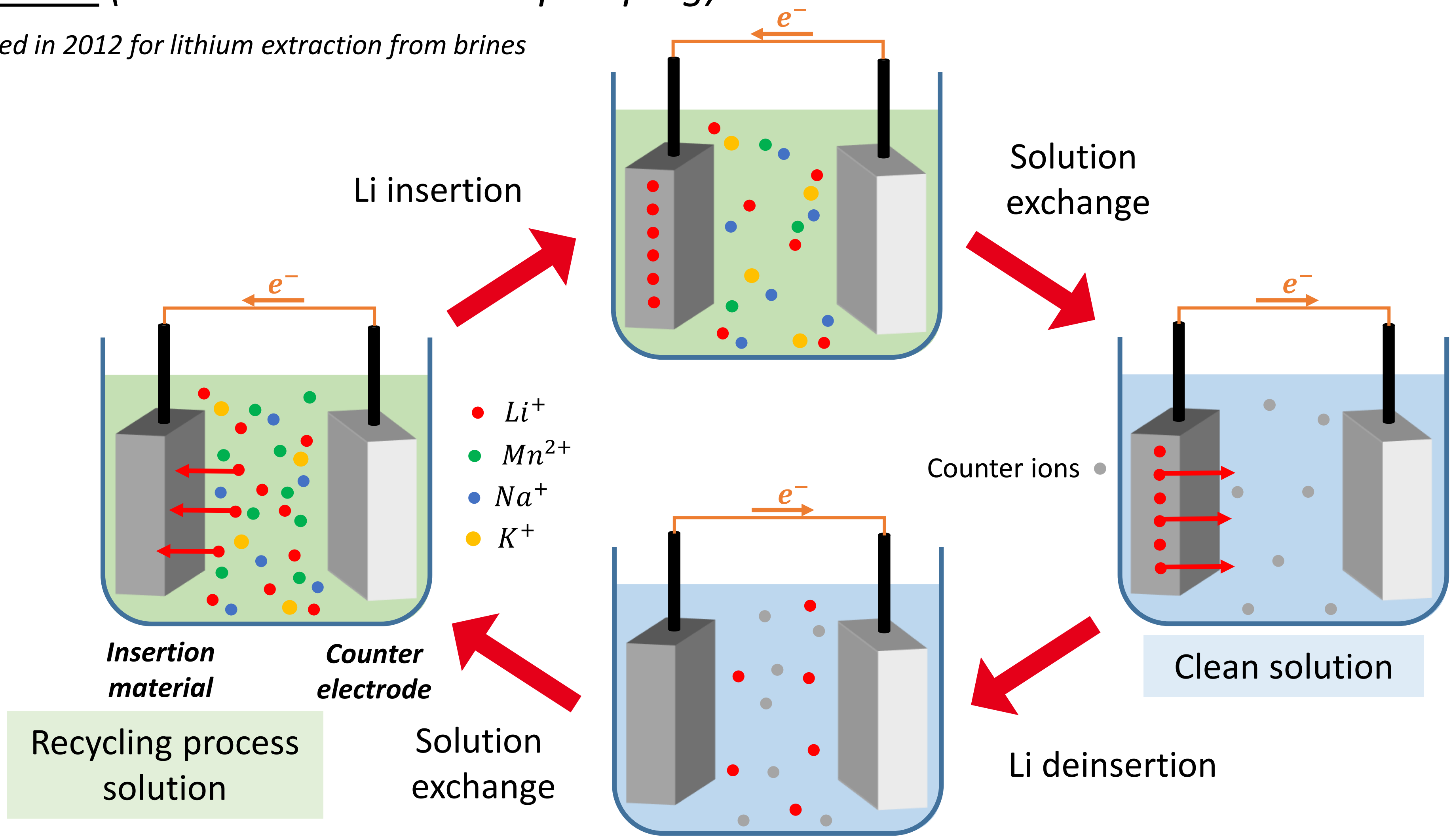
Focus : Study of ELIP process

Xu, Ping et al, Journal of Material Science, 2020
Pasta, Battistel, Mantia, Energy Environ. Sciencs 2012
Zhao, Zhong-Wei et al, Transactions of Nonferrous Metal Society of China, 2013

State of the art: ELIP process

Concept of ELIP *(Electrochemical Li ion pumping)*

Process developed in 2012 for lithium extraction from brines

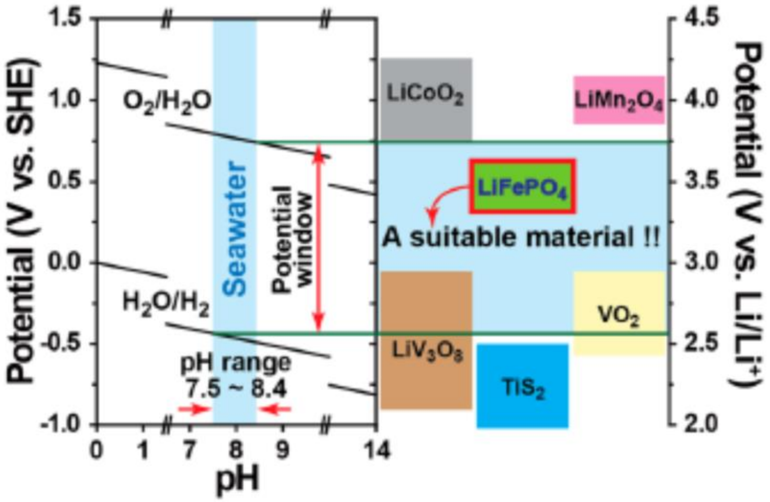


Goal : Use ELIP for battery recycling

State of the art: ELIP material

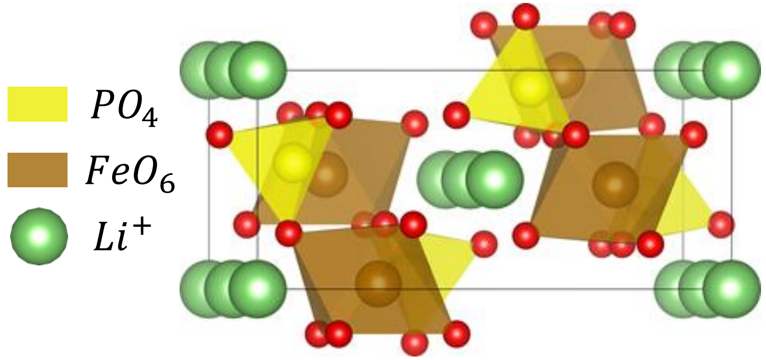
Material choice for ELIP process

All possible insertion materials → Li selectivity, Water stability, Filter, Knowledge, Cost → **LFP**



E-pH diagram, stability domains in water of certain electrode materials

LFP : $LiFePO_4$



Olivine structure along the zone axis [010]

Study of LFP as the insertion material

J. Poulizac, thèse, 2022

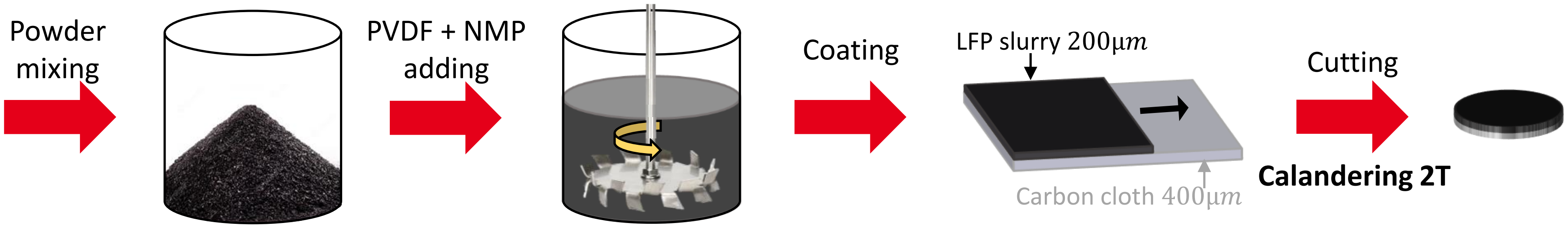
Experimental – 3 electrodes setup

Electrode production:

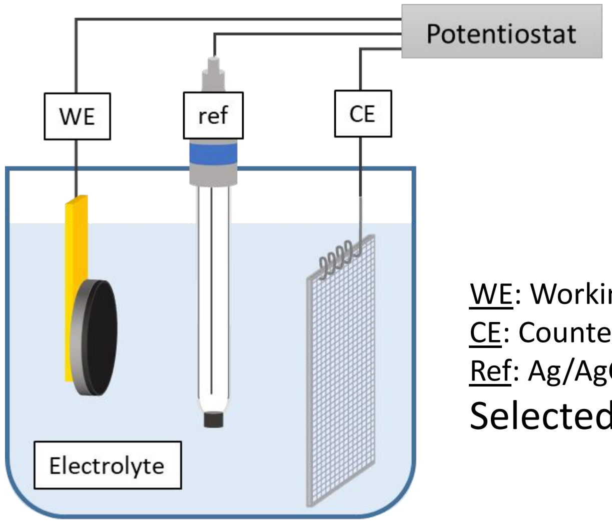
Coating synthesis method

Active material : $\boldsymbol{LiFePO_4}$
+ e^- conductor : $C\ Super\ P$
+ Binder : $PVDF$
+ Solvant : NMP

Selected substrate : **carbon cloth**



3-Electrodes set up:



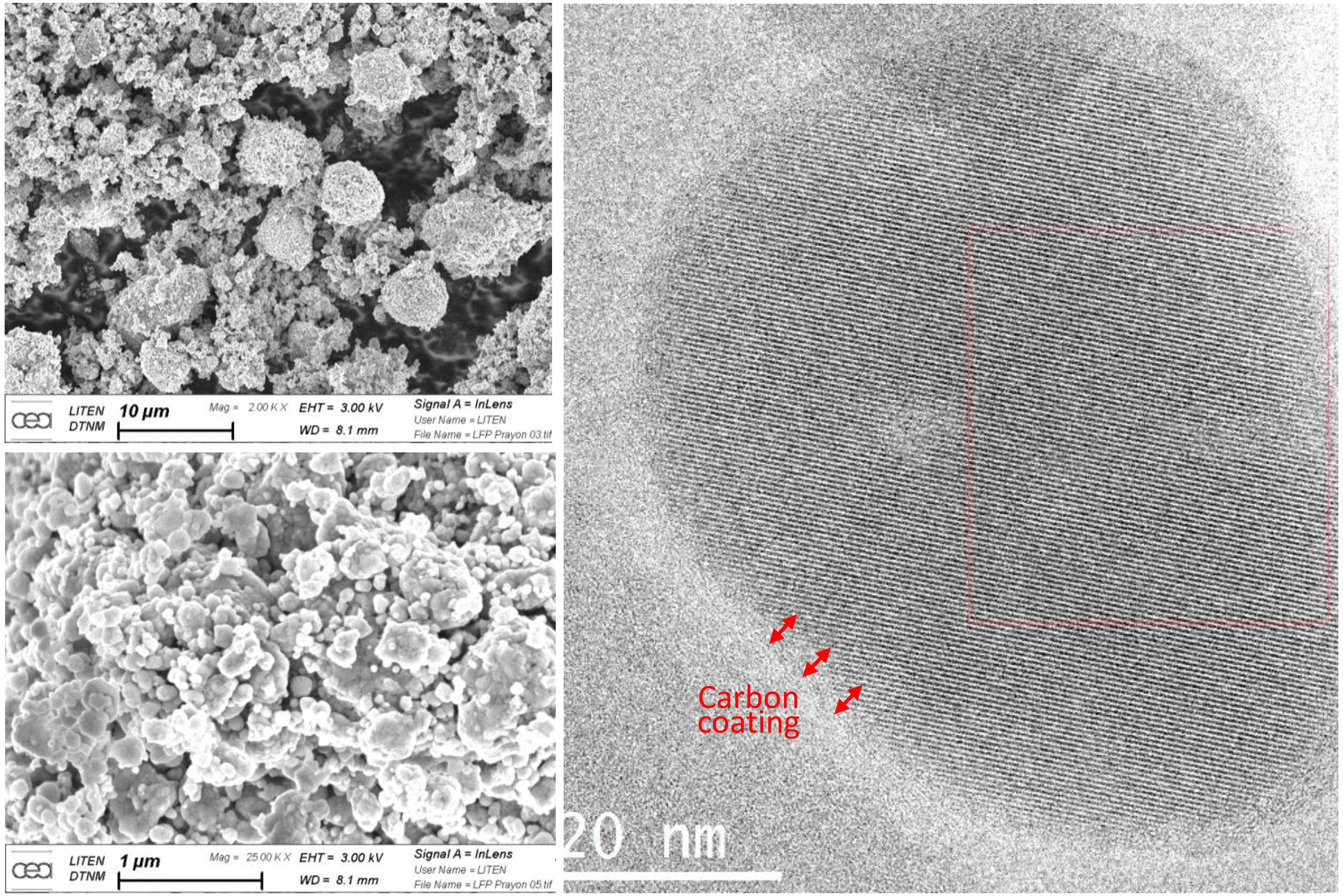
3 electrodes setup

WE: Working Electrode
CE: Counter Electrode: Platinium grid
Ref: Ag/AgCl with saturated KCl reference electrode

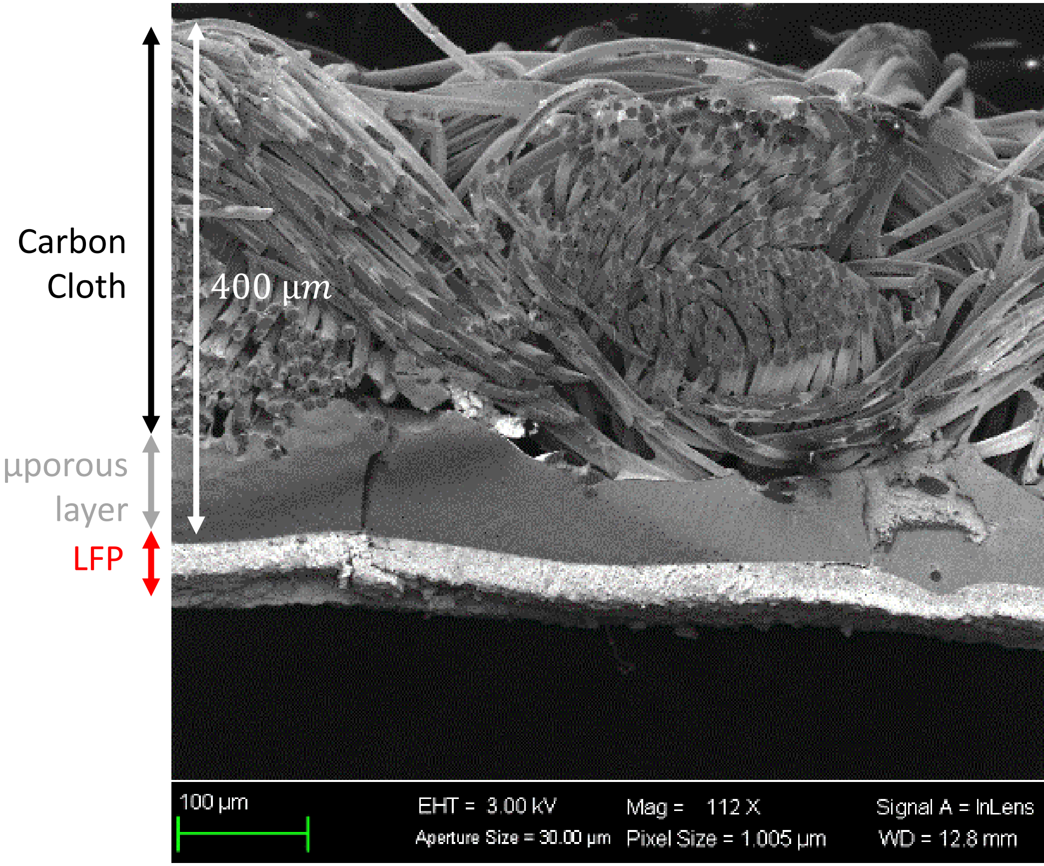
Selected electrolyte : $\boldsymbol{LiNO_3\ 0.5M}$

Experimental – 3 electrodes setup

Microscopic characterization:



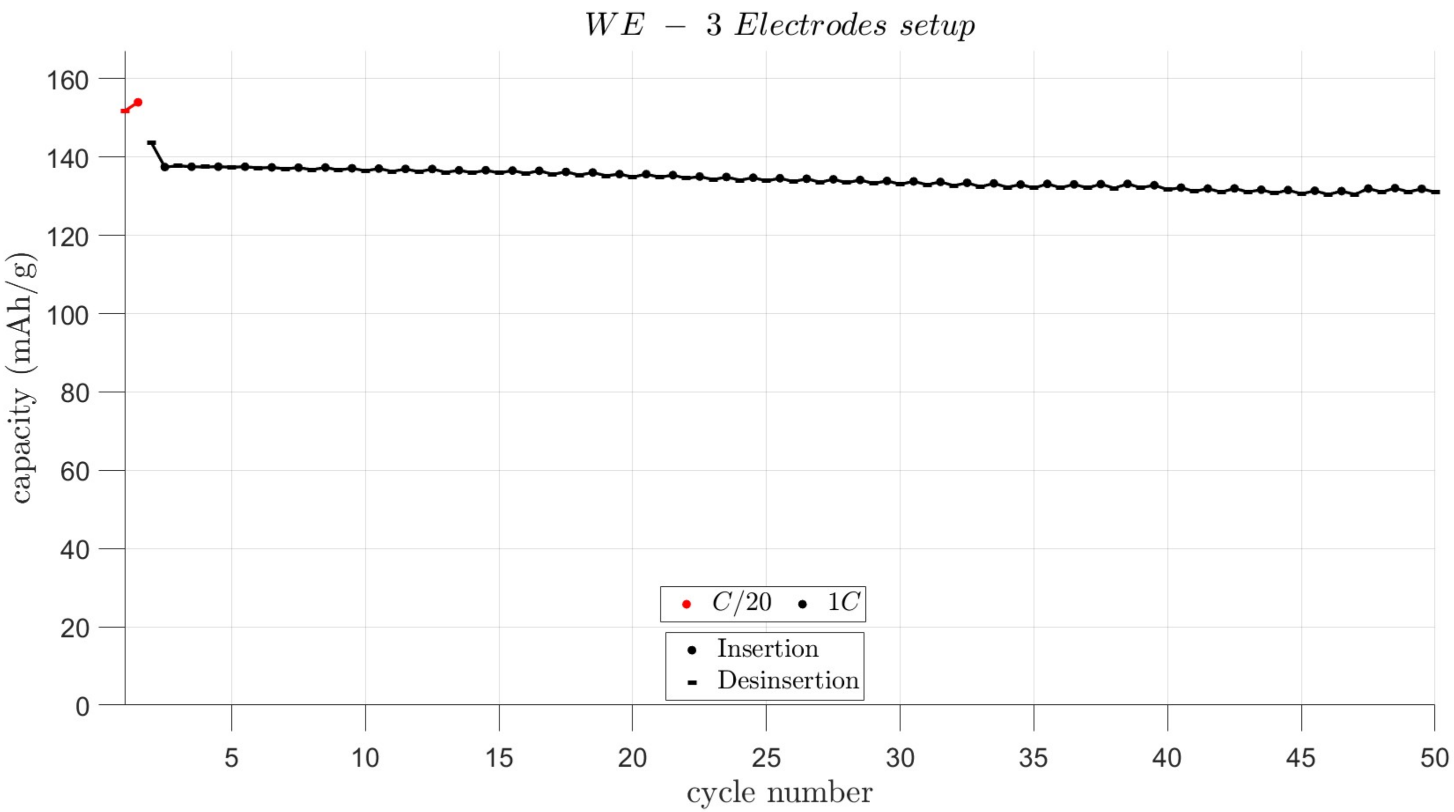
MEB and HRTEM images of LFP powder



MEB image : cross-section of LFP onto CC electrode

Experimental – 3 electrodes setup

Study of capacity



WE capacities as a function of cycling

- ☑ Initial capacity ~150mAh/g

(theoretical capacity: 170 mAh/g)

(state of the art: between 130 and 165 mAh/g)

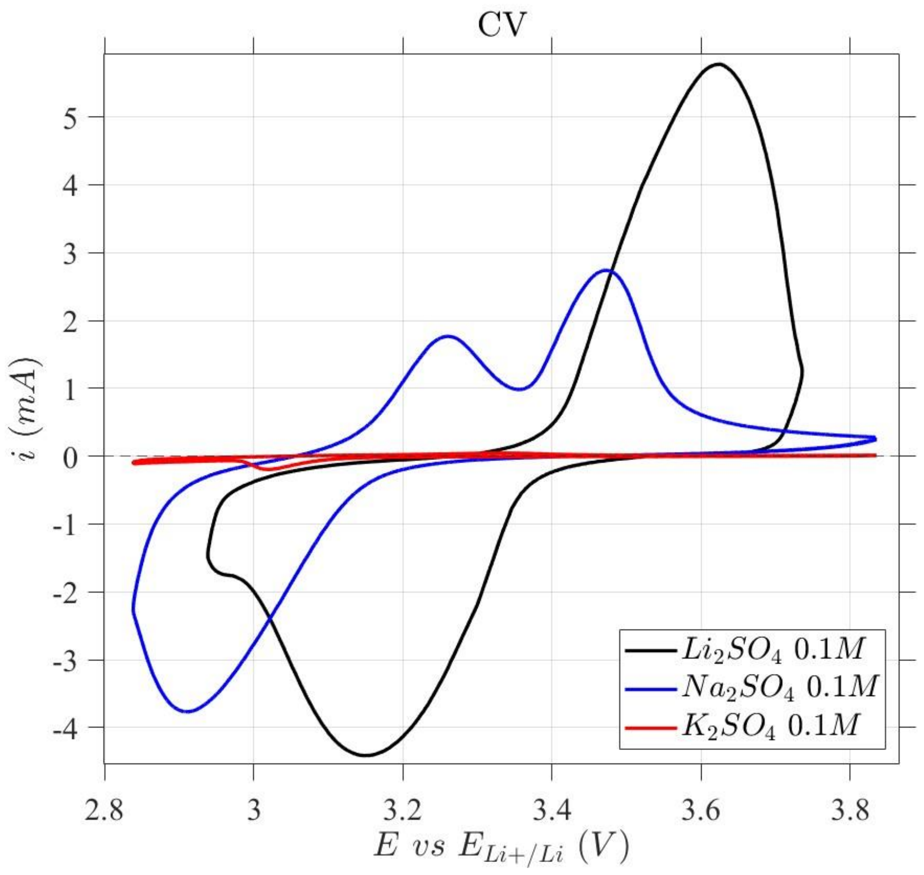
- ☑ Reproducibility : OK
- ☑ Durability : OK

These electrodes are sufficient for conducting more in-depth studies

Zeng, Electrochim. Acta, vol. 177, pp. 277–282, 2015
Yin, Chin. J. Chem. Phys., vol. 28, no. 3, pp. 315–322, 2015
Yesibolati, Electrochim. Acta, vol. 152, pp. 505–511, 2014

Experimental – 3 electrodes setup

Study of selectivity



Normalized E-I curves of delithied LFP in different electrolyte

C-rate C/2	Capacity mAh/g	Ion radius Å
$LiNO_3$ 0.5M	150 ± 5	0.9
$NaNO_3$ 0.5M	110 ± 10	1.16
KNO_3 0.5M	7 ± 3	1.52

Capacity of delithied LFP in different electrolyte (mAh/g)

	C-rate	Li selectivity
Li vs Na	3C	$98.3\ \% \pm 1$
	C	$98.7\ \% \pm 0.5$
	C/10	$99.5\ \% \pm 0.1$
Li vs K	C/2	~ 100

Selectivity (percentage of Li inserted) of the electrode during cycling at different C-rate in equimolar electrolyte

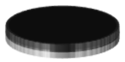
Good selectivity with K and Na, can be optimized

R. D. Shannon, Acta Cryst, vol. 32, p. 751, 1976

Coin cell production

Manufacturing protocols for coin cells

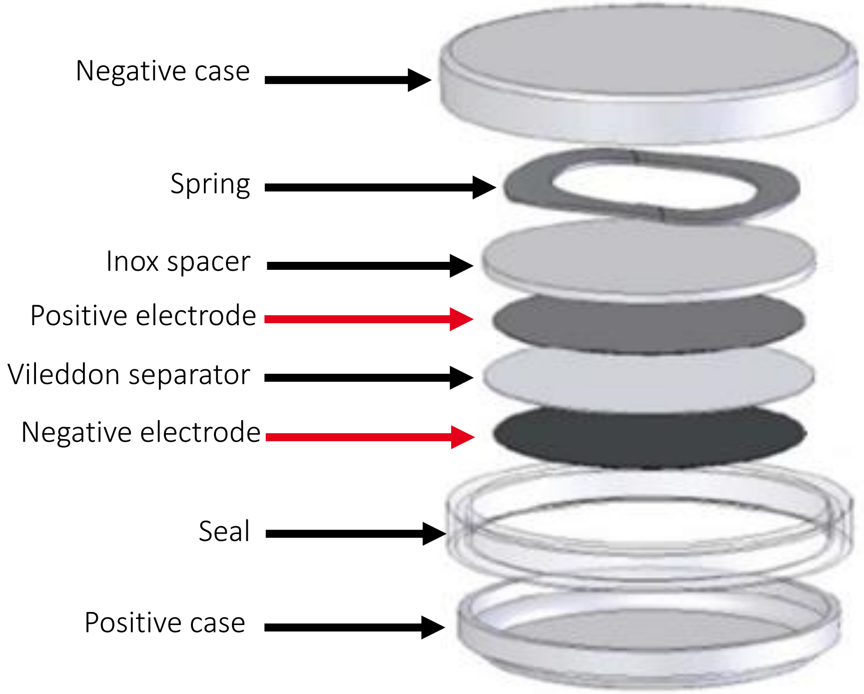
→ Working Electrode of interest : LFP — enduction →



→ Counter Electrode : ~~$Li_{métal}$ or Pt counter electrode~~ ?

Delithied LFP electrode, with $Capa_{CE} \gg Capa_{WE}\ (mAh)$

LFP —chemical delithiation→ $Li_{x=0.2}FePO_4$ —enduction→



→ Electrolyte : $LiNO_3\ 0.5M$

Coin cells characterisation :

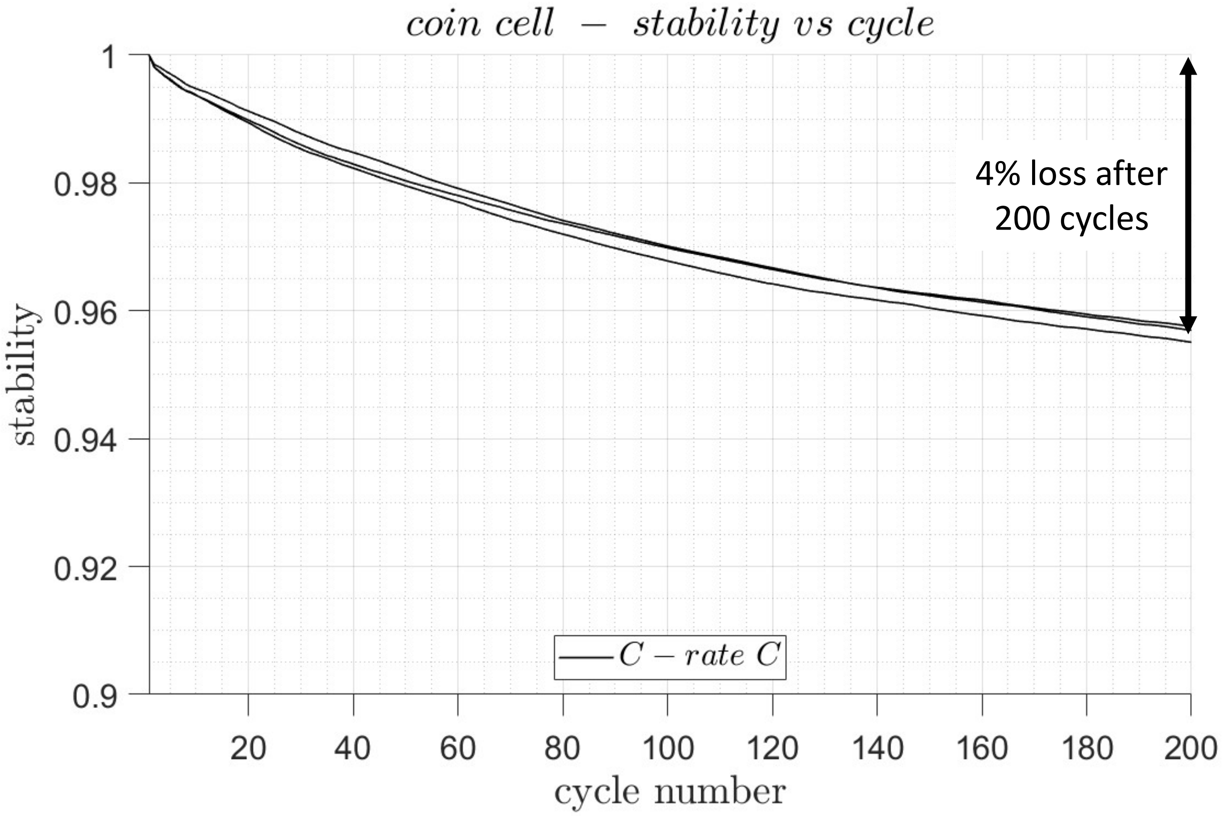
☑ Good reproducibility of coin cells

☑ Equivalent capacities with both setup

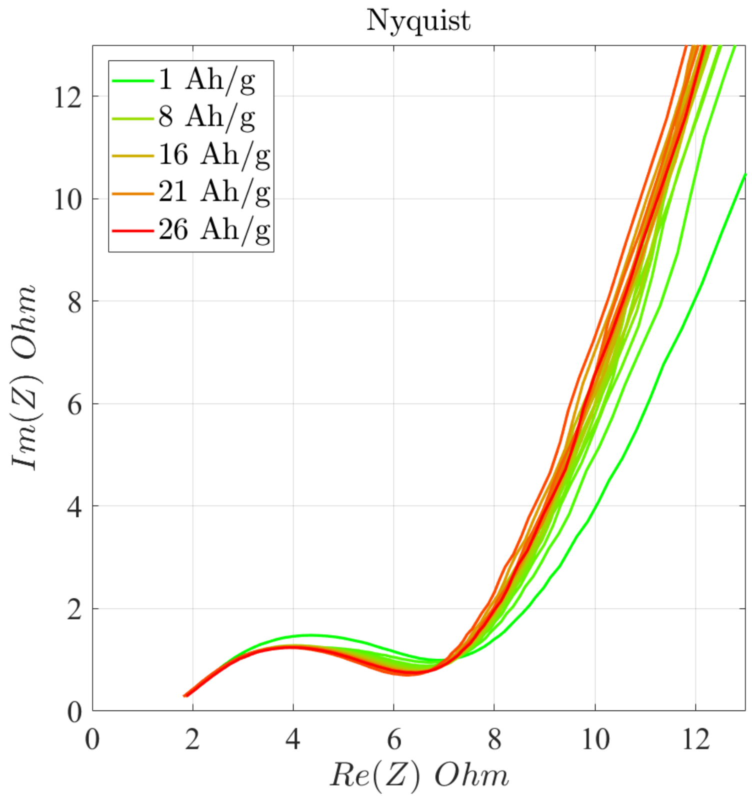
Coin cell setup can be used to study our LFP electrodes

Coin cell cycling

Study of stability



Electrode stability as a function of cycling at Crate C



Nyquist graph evolution of a PB during 1C cycling

Good stability of the electrodes in aqueous electrolyte

Objective : understanting degradation mechanisms

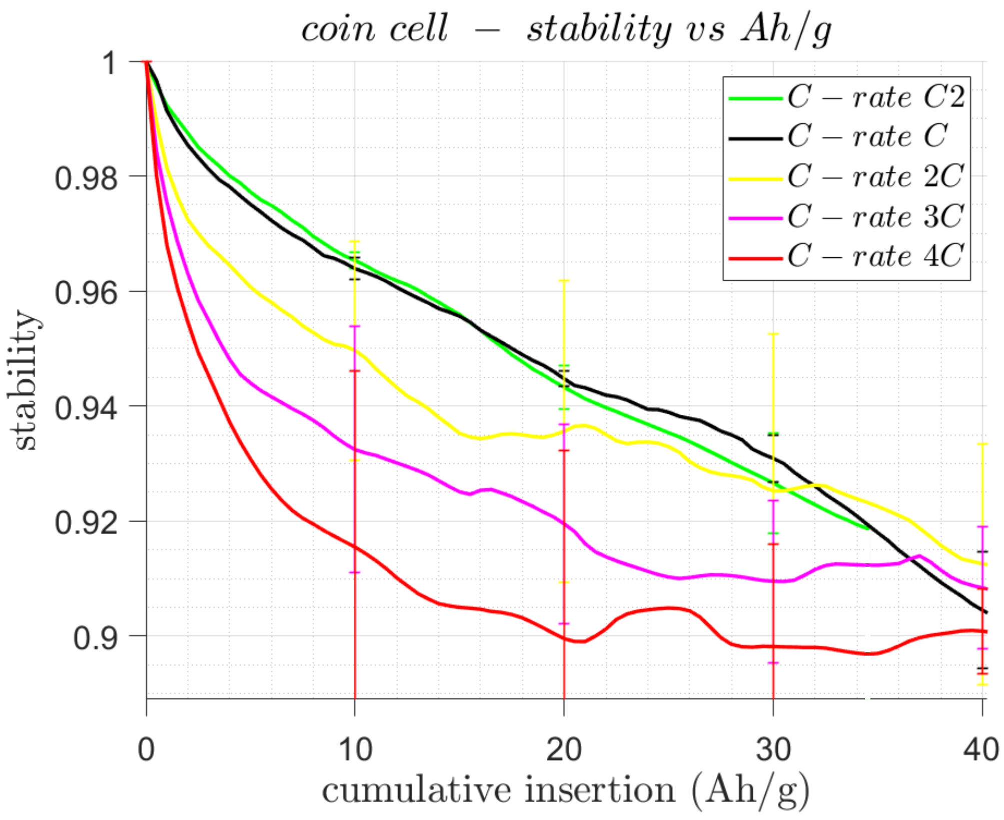
93% *after 100 cycles at 1C : Tron, doi: 10.1021/acsami.6b16675*

~80% *after 200 cycles at 1C : Zeng, doi: 10.1016/j.electacta.2014.12.088*

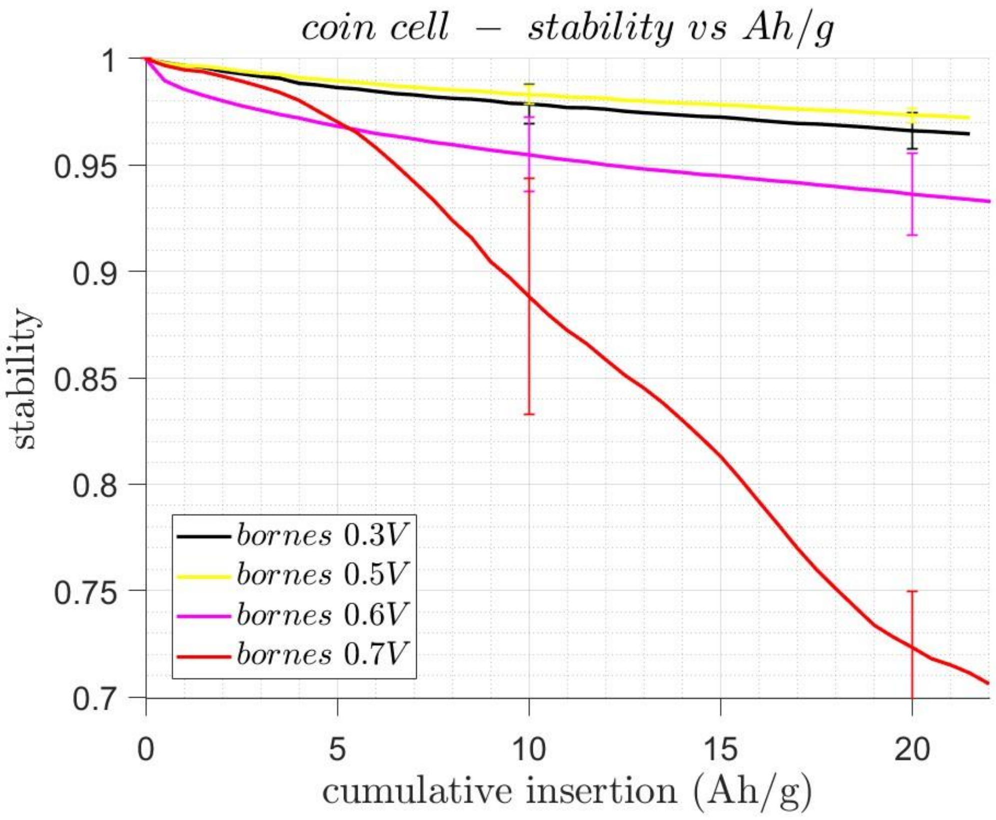
Coin cell cycling

Study of stability

→ Change cycling parameters to accelerate/understand degradations



Averaged electrode stability as a function of cumulative insertion (Ah/g) for different C-rate, E bornes = ±0.3V



Averaged electrode stability as a function of cumulative insertion (Ah/g) for different E bornes, C-rate = C

Objective : coupling PEIS – DRX – HRTEM – Electrochemistry to understand degradation mechanisms

Conclusions and perspectives

☑ Synthesis of high-performance electrodes in aqueous environments

- *capacity*
- *selectivity*
- *stability*

☑ Development of coin cell for aqueous electrolyte

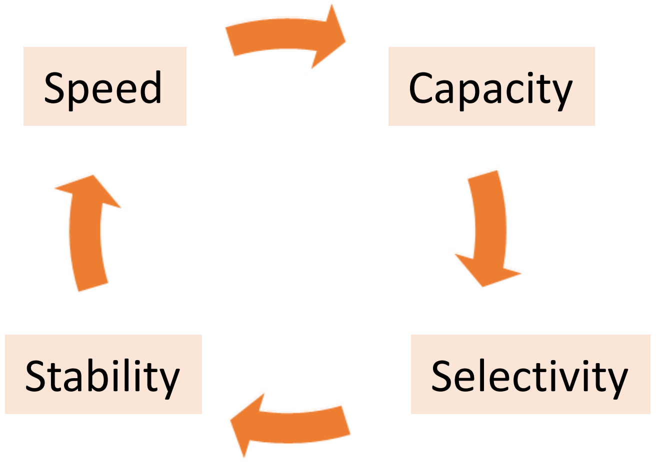
<u>Ongoing studies :</u>

→ Understand degradation mechanisms

Coupling electrochemical characterisation with HRTEM, EELS, DRX, PEIS

→ Electrode performance (in complex electrolytes)

→ Final goal : find the right balance



Thanks