Electrochemical Lithium Extraction Applied To Li-ion Battery Recycling

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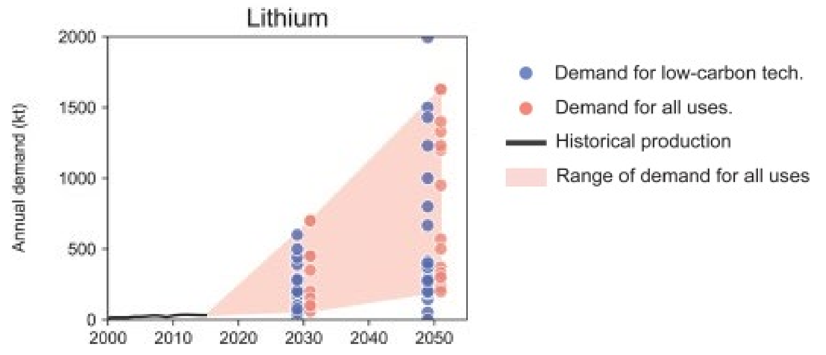
Outline

Lithium recycling in figures

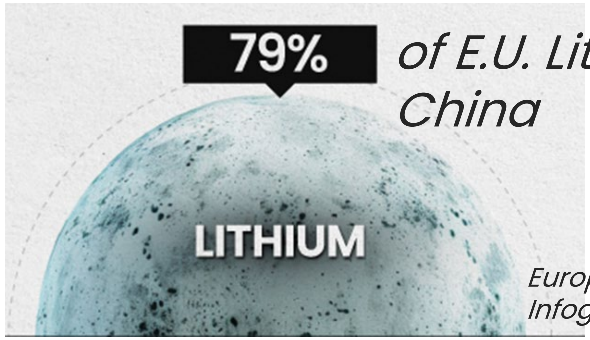
An essential technology

A forecast increasing demand



Watari, T. *et al., Resources, Conservation and Recycling* **155**, 104669 (2020).

Geopolitical context



of E.U. Lithium comes from China

European Comission, Bloomberg 2024
Infography by elements.visualcapitalist.com

2021

Only 

of Li recycled in the world

IEA / Infography by elements.visualcapitalist.com

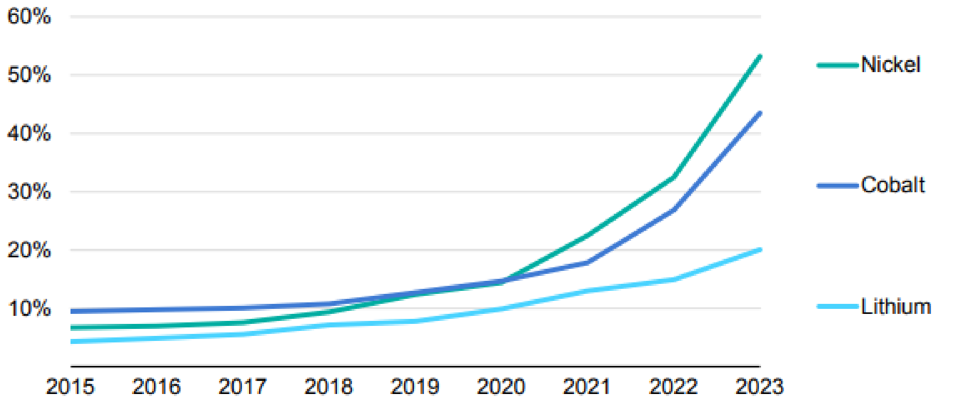
2023 : **1st E.U. directive on Li recycling**
50 % of Li recycled by **2027**
6 % of recycled Li in batteries by **2031**

➢ **Need for performant Li-recycling methods !**

State-of-the-art of lithium recycling

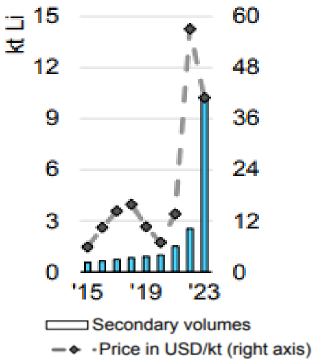
Lithium recycling rate is growing worldwide…

Figure 1.4 **Recycling rates of battery lithium, nickel and cobalt from available battery recycling feedstock**



IEA. CC BY 4.0.

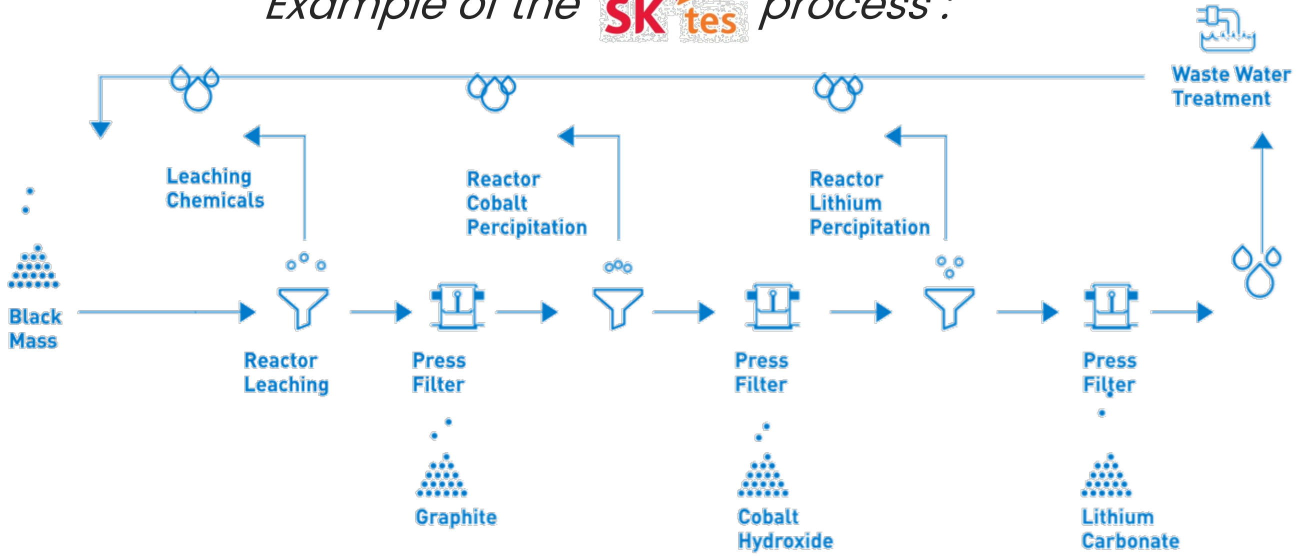
Notes: These recycling rates refer to the recovered metals from all battery secondary sources over the metals contained in the available recycling feedstock from all battery secondary sources (including manufacturing scrap and end-of-life batteries). Includes manufacturing scrap and end-of-life batteries from portable electronics, e-bikes, EVs, and maritime and storage applications.
Sources: IEA analysis based on data from Circular Energy Storage, Benchmark Minerals Intelligence and Project Blue.



Recycling of Critical Minerals, IEA Report, 2024

… through hydrometallurgical-type processes

Example of the SK tes process :



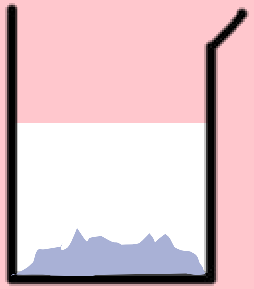
Increasing demand for recycling

Improvements of the recycling process are required :

- Improve the process **efficiency**
- **Decrease** the use of **hard chemicals**
- Decrease the **effluent** amount and/or improve their treatment

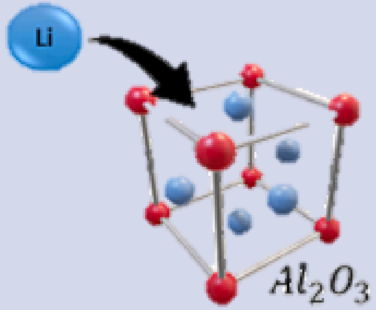
Extraction and recyling methods for lithium

Precipitation



pH adjustement to precipitate Li salts

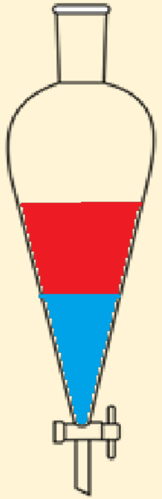
Adsorption



Al_2O_3, MnO_2 …

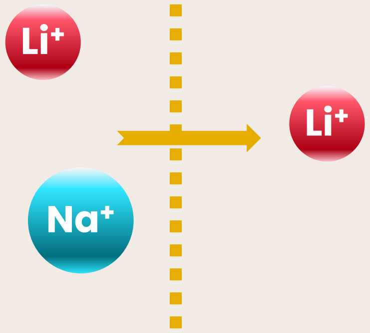
Li^+ adsorption in the materials and acid regeneration

Solvant extraction



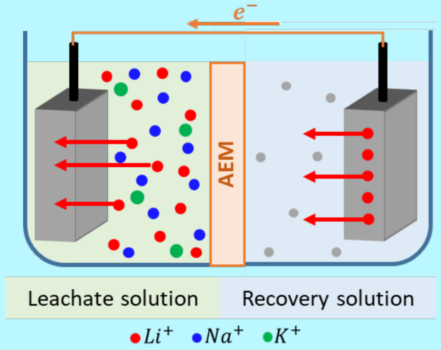
Liquid-liquid extraction

Membranes



Filtration on a lithium-selective membrane

Electrochemical methods



Use of an external current or tension to selectively extract Li^+

Methods used for Li extraction from brines AND recycling

Outline

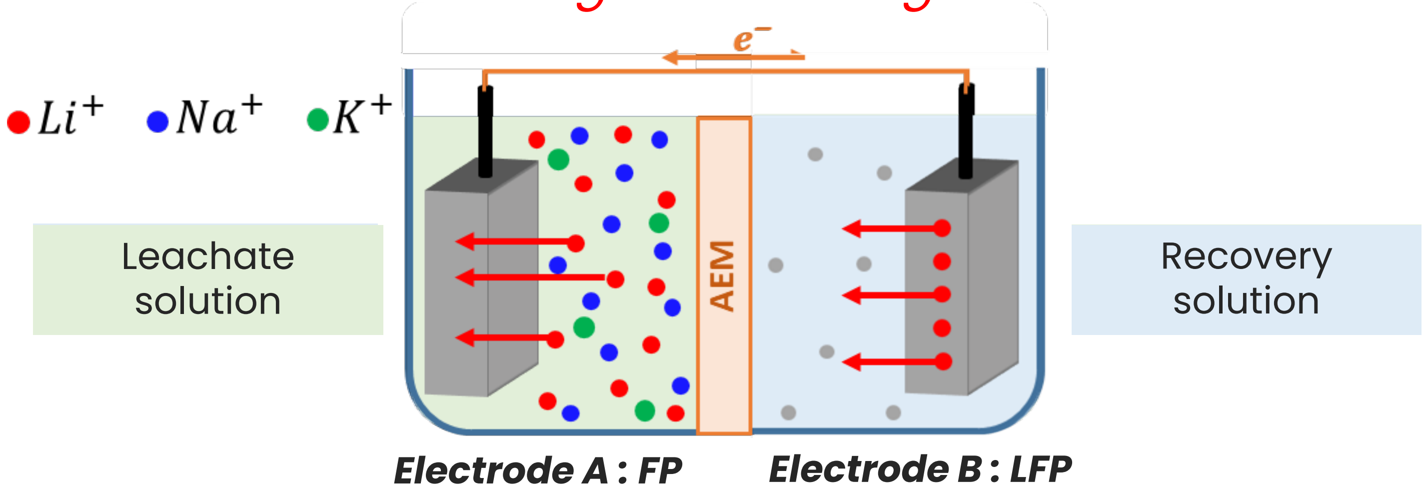
Electrochemical Lithium-Ion Pumping (ELIP)

Process presentation

- Many possible configurations :

Symmetrical (« Rocking-Chair ») **vs** Asymmetrical **vs** Electrosorption (Selective membranes)

Rocking-Chair Configuration :

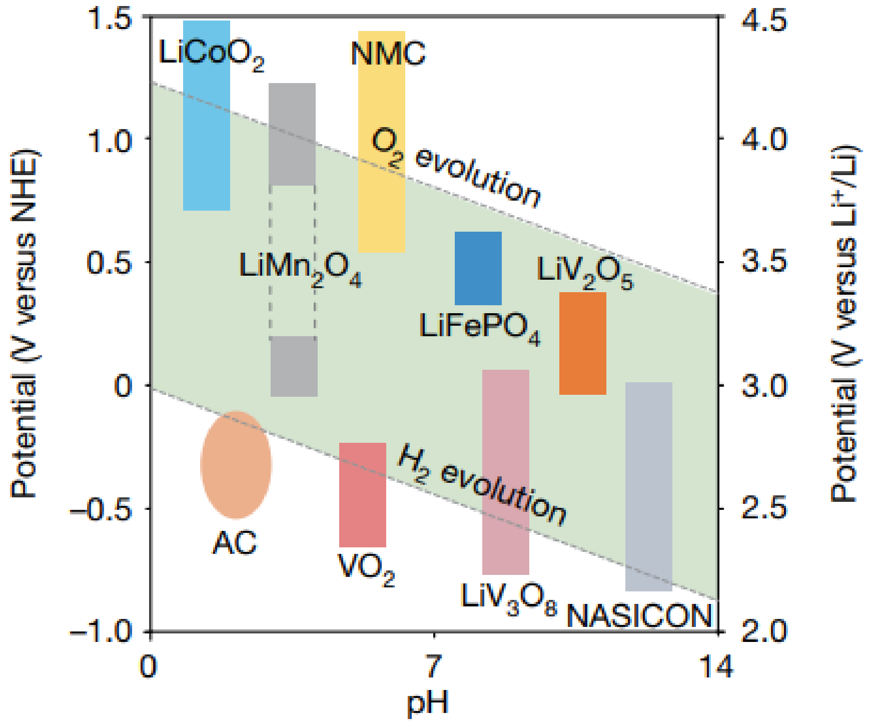


- Developped for brines
  - **To adapt to Li recycling : different challenges**
    - Na and K selectivity (from previous steps)
    - Organic polluants in the recycling mix ?

Suu, L. *et al.,* Advances in electrochemical recovery of valuable metals: A focus on lithium. *Desalination* **612**, 118960 (2025).
Wu, L. *et al.* Lithium recovery using electrochemical technologies: Advances and challenges. *Water Res.* **221**, 118822 (2022)

Electrochemical Lithium-Ion Pumping (ELIP)

What are the possible active materials ?



Yang, S., Wang, Y., Pan, H., He, P. & Zhou, H. Lithium extraction from low-quality brines. Nature 636, 309–321 (2024).

Conditions

- ➢ Selective insertion of Li
- ➢ Stable in the electrochemical stability window of H_2O

Few examples

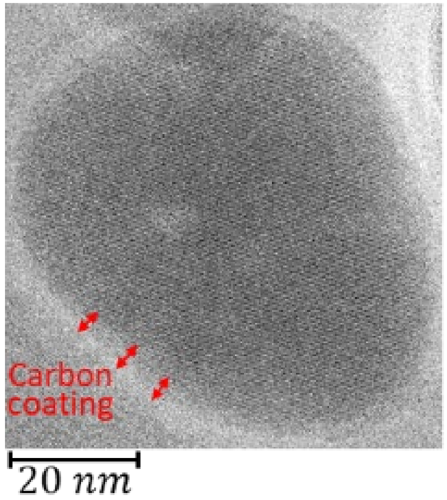
	Advantages	Drawbacks
$LiFePO_4$	Low cost Low toxicity No critical material	Na co-insertion Olivine (1D diffusion)
$LiMn_2O_4$	Low cost No critical materials No Na/K co-insertion Spinel (3D diffusion)	Low stability due to Mn^{2+} dissolution
$LiCoO_2$	High theoretical specific capacity	Low stability H_2O Contains Co Na insertion
LiV_2O_5	High theoretical specific capacity	Dissolution Na insertion

Outline

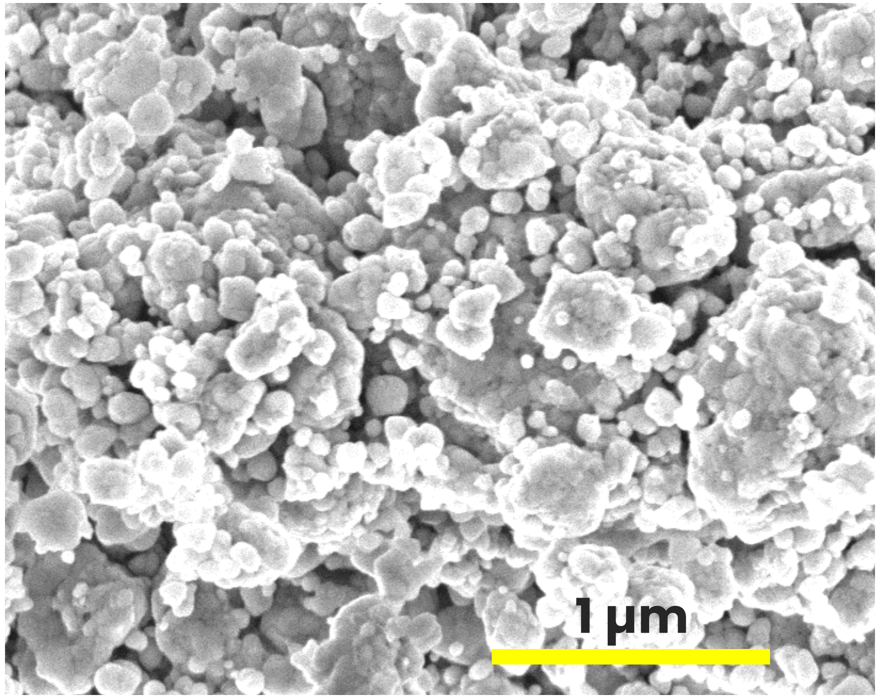
1. **Status update on lithium recycling**
   And why are we focused on electrochemical methods
2. **Electrochemical Lithium-Ion Pumping (ELIP), a method of interest**
   About the process
3. **$LiFePO_4$ vs $LiMn_2O_4$: olivine vs spinel**
   What differences ? What relative advantages ?
4. **ELIP proof-of-concept with $LiFePO_4$**
   A first H-Cell to demonstrate the enrichment of a recycling solution
5. **Conclusions & following of the project**

Materials comparison for ELIP

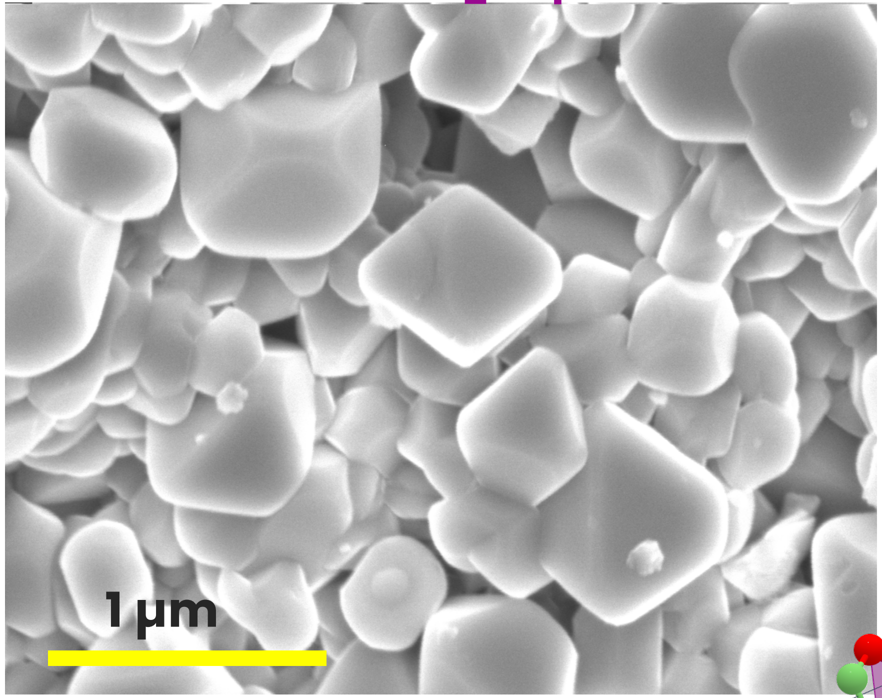
Physico-chemical differences

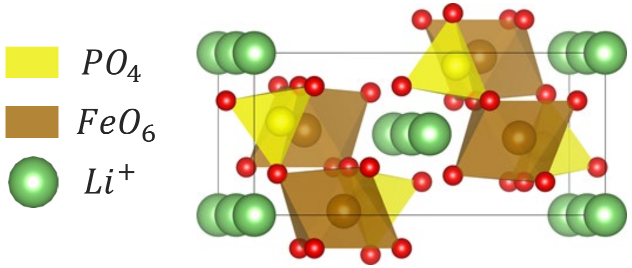


$LiFePO_4$



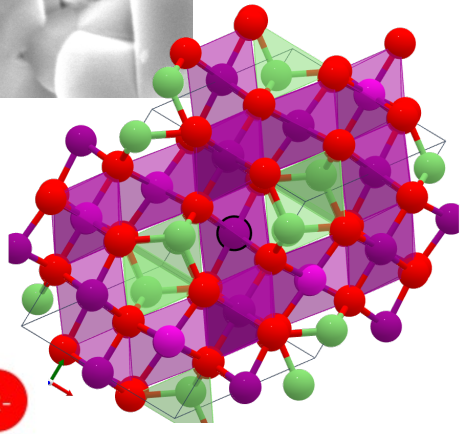
$LiMn_2O_4$





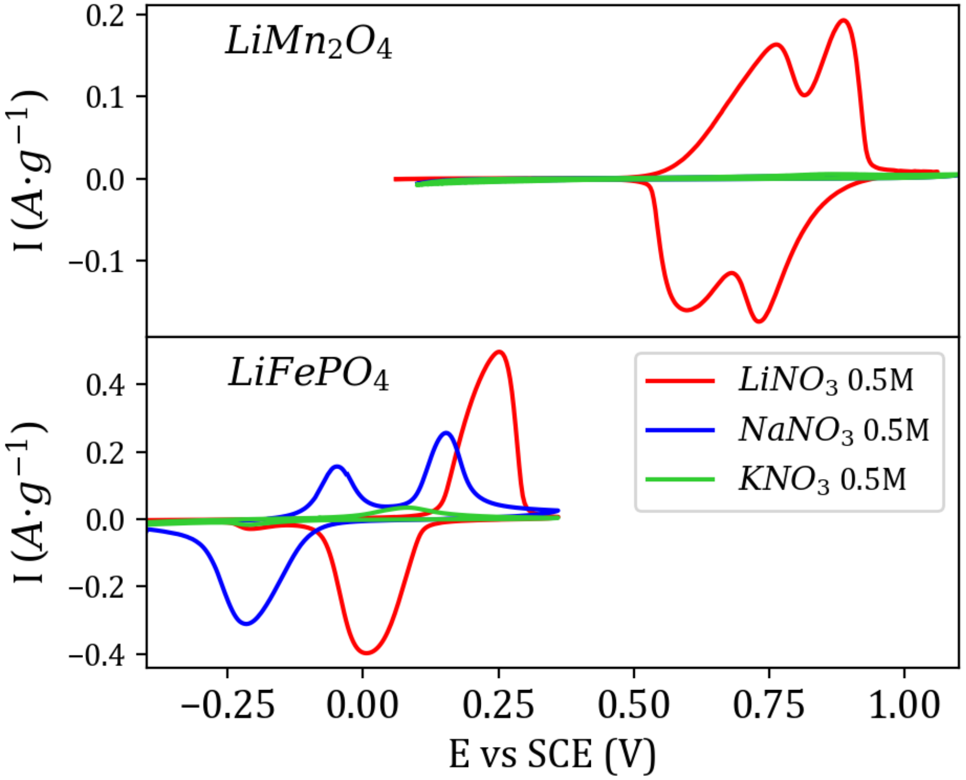
Olivine structure
→ 1D Li-diffusion

Spinel structure
→ 3D Li-diffusion



Materials comparison for ELIP

Cyclic voltammetry with different cations



Selectivity

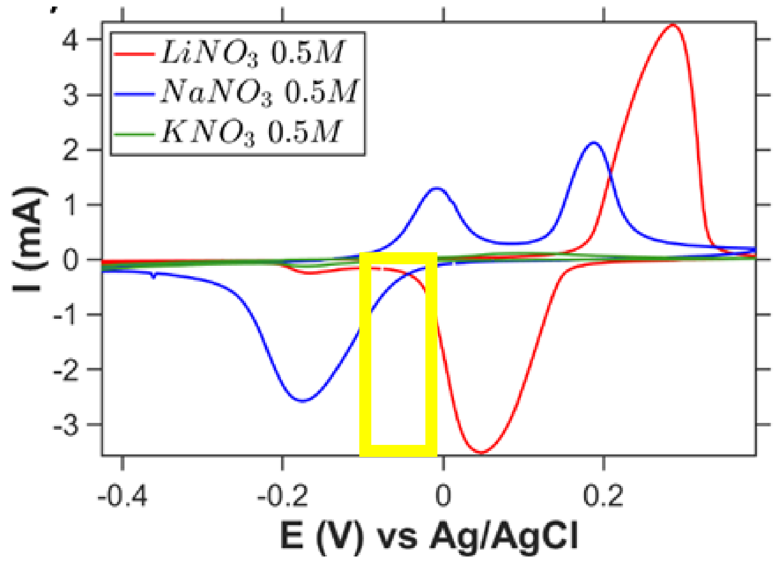
- $LiMn_2O_4$ only inserts Li^+
- $LiFePO_4$ also inserts Na^+, K^+

Potential window

- $LiMn_2O_4$ lithiation potentials are between 0,5 and +1V
  - Close to water oxydation (E°=0,5 V vs SCE at pH7)
- $LiFePO_4$ lithiation potential is between −0,3 and +0,3 V
  - Close to dissolved O_2 reduction (E°=0,1 V vs SCE)

Raising selectivity in LFP

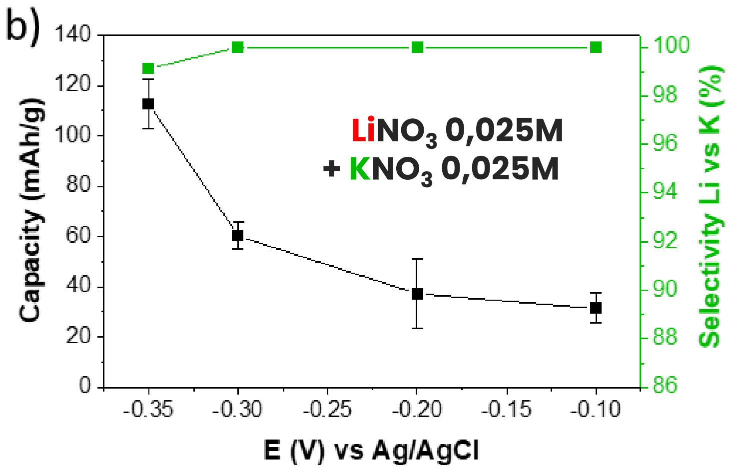
By playing with electrochemical parameters

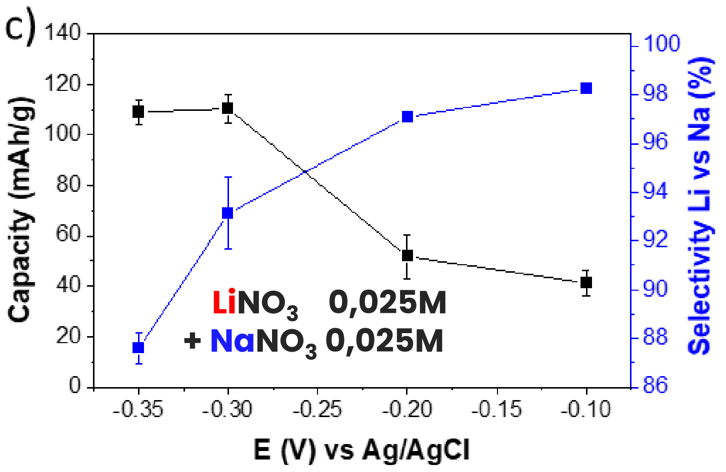


- ➢ Li and Na insert at different potentials

Testing different discharge cutting potentials

Chronopotentiometry at C/2

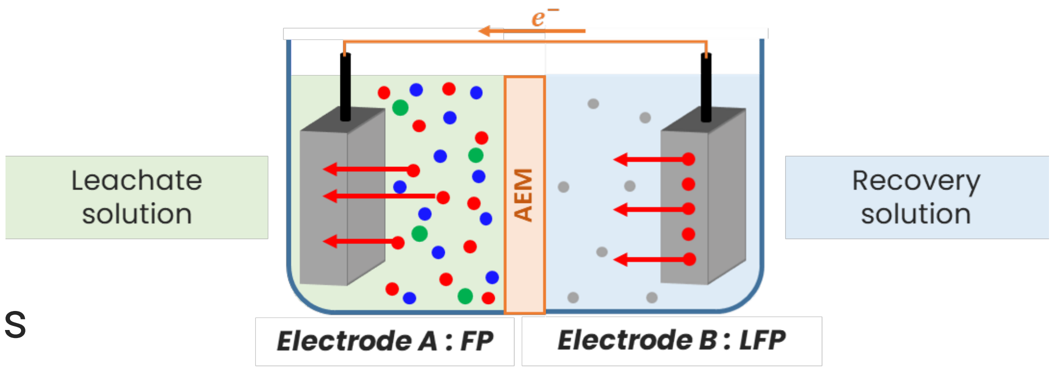




- ➢ Possibility to **increase selectivity** of LFP
- ➢ *The cost is a decrease of the capacity*

Materials comparison for ELIP

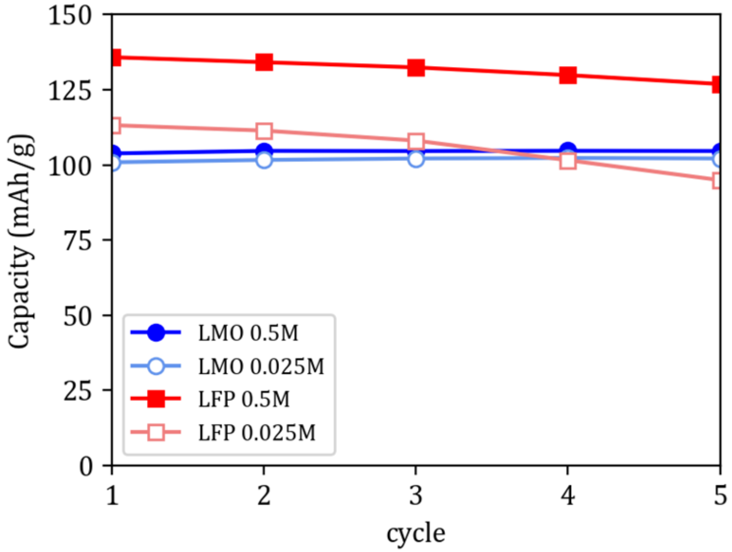
The effect of Lithium dilution

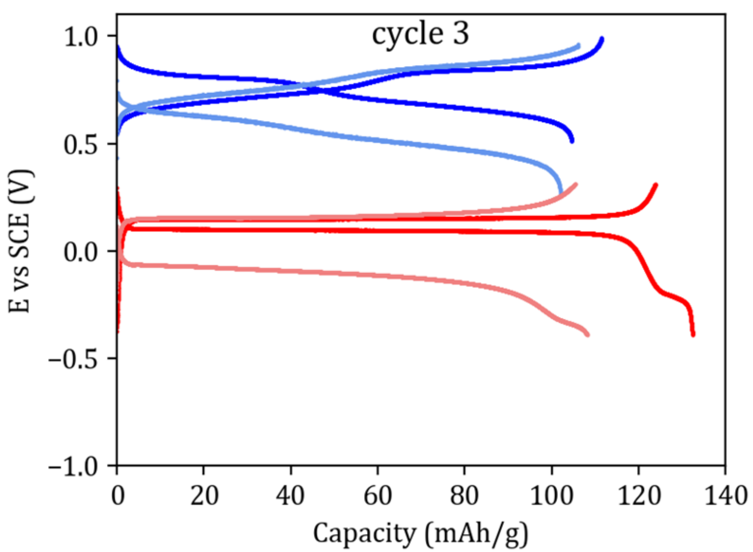


At the end of the ELIP process, the solution will be low concentrated in Li^+ :

➢ The material should work at low Li^+ concentrations

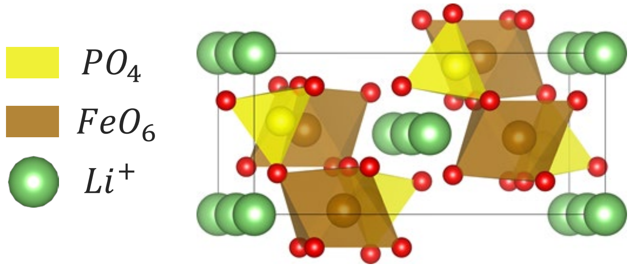
Chronopotentiometry of LMO and LFP at different Li^+ concentrations :



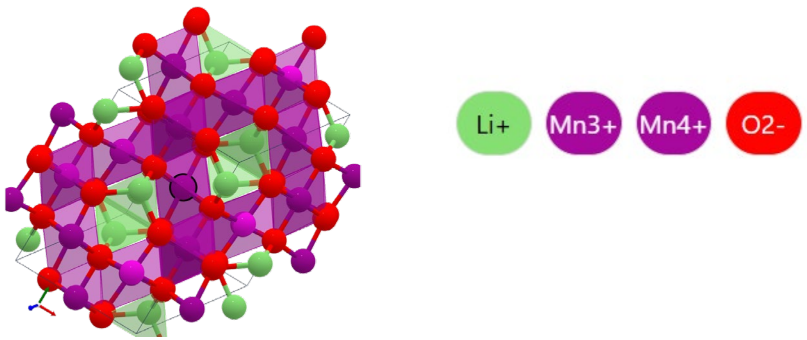


- $LiMn_2O_4$ shows better stability at low concentration in $LiNO_3$
- Both reduction plateaus are lowered because of Li low concentrations
  - ➢ LFP plateau is closer to O_2 reduction plateau

Olivines vs. Spinels : complementary materials



LFP vs. **LMO**



Higher capacity
- ➢ Highest Li quantity recycled

Lower toxicity and price
- ➢ Easiest to integrate in an industrial process

Theoretically better selectivity
- ➢ To be confirmed with chemical analysis

Better performance in low-concentrated electrolyte
- ➢ Best for ELIP

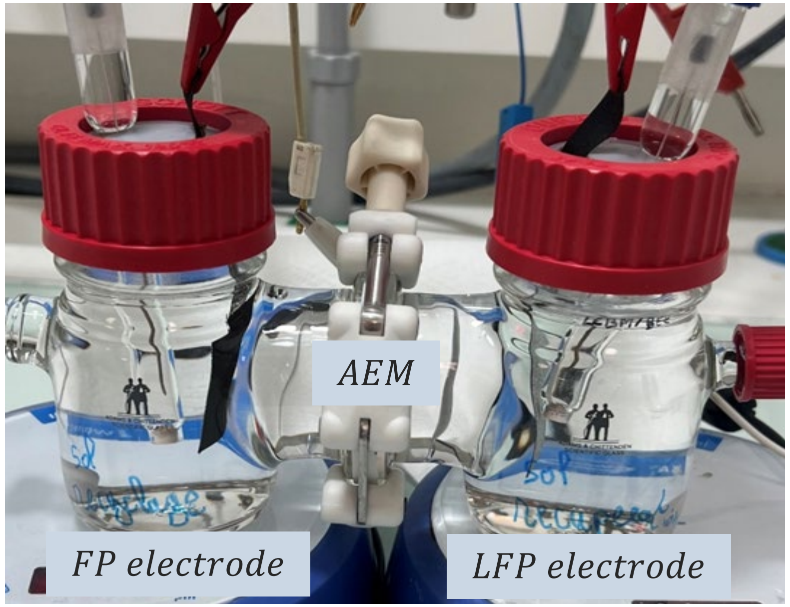
➢ Both materials show advantages and drawbacks

➢ Further experiments running for quantifying selectivity

Outline

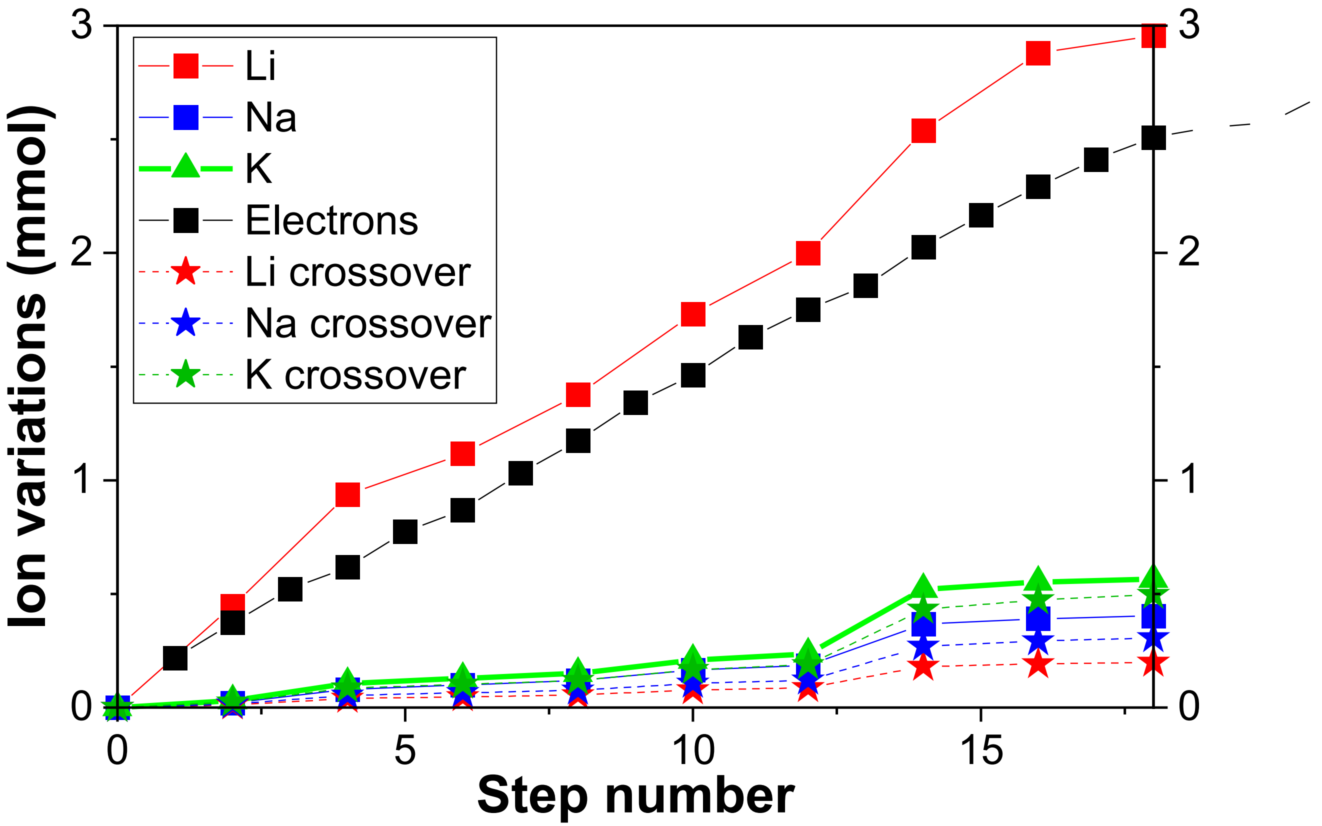
A first proof of concept for ELIP in CEA-Grenoble

Li	0.1 *M*	0.7 g/L
Na	0.1 *M*	2.3 g/L
K	0.1 *M*	3,9 g/L



Recovery solution

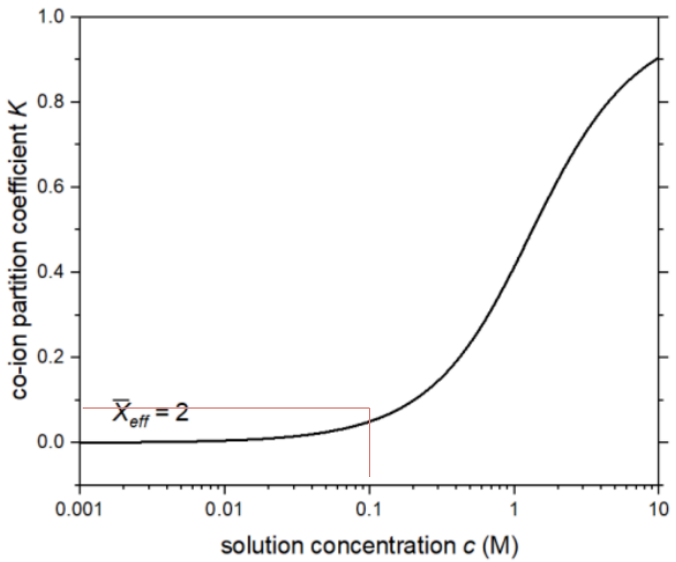
Li	0.05 *M*	0.35 g/L



- Li^+ enrichment of a recovery solution
- But other cations concentrations also increase… why?

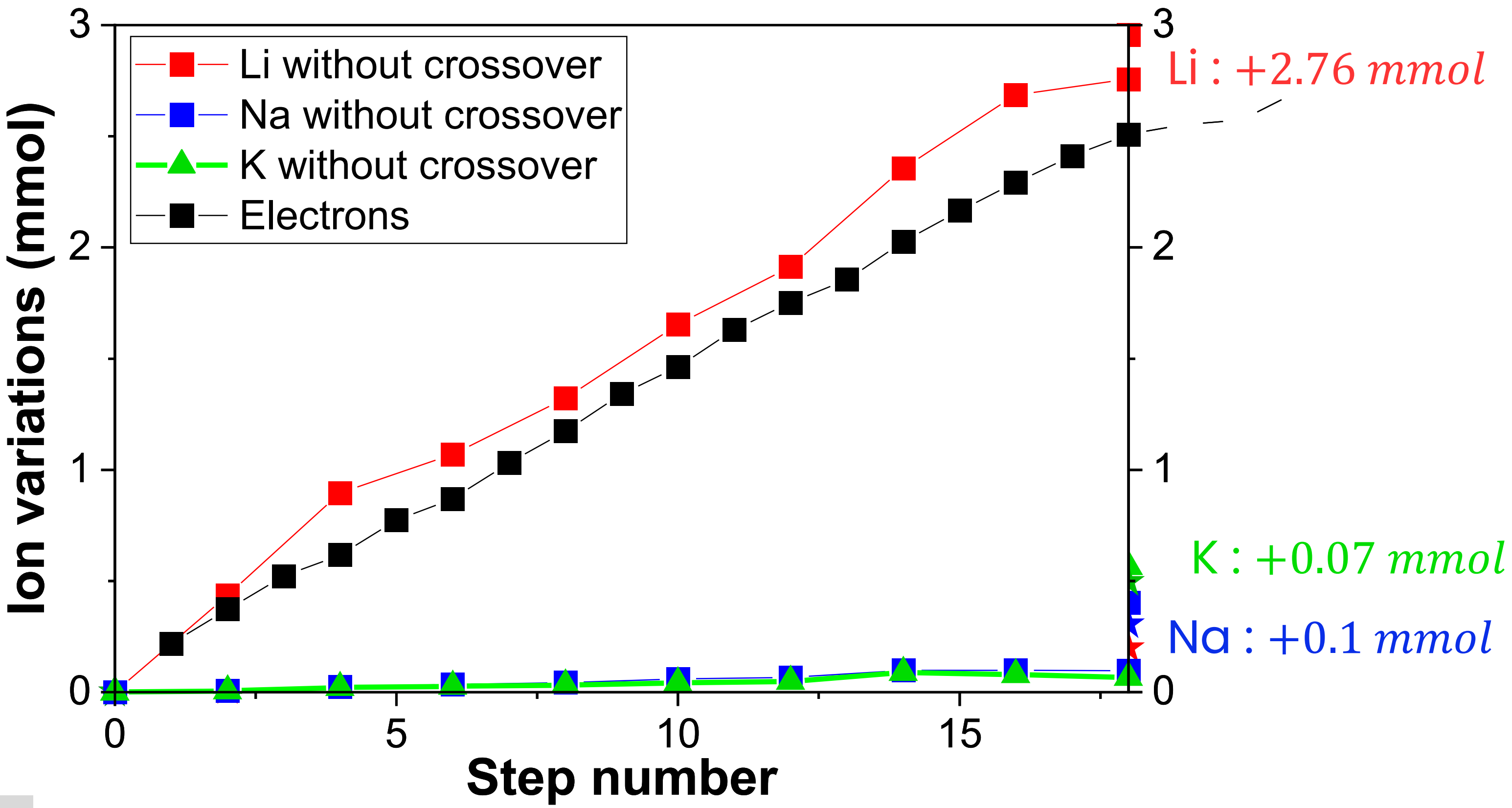
A first proof of concept for ELIP in CEA-Grenoble

About cation crossover



$$K_c = \frac{c_c^m}{c_c^s} = -\frac{\overline{X_{eff}}}{2c_c^s} + \sqrt{1 + \left(\frac{\overline{X_{eff}}}{2c_c^s}\right)^2}$$

c_c^m	Cation concentration in the membrane
c_c^s	Cation concentration in the solution
$\overline{X_{eff}}$	Effective fixed charge density in the membrane, $\overline{X_{eff}} = r \cdot IEC \cdot \rho$ with r being the ratio of ions participating the transport, IEC being the ion exchange capacity and ρ the membrane density.



- **The membrane is permeable** to co-cations the more the cation concentration increases
- **This phenomenon can be decreased** by adjusting membrane parameters (density, IEC)

El-Nagar *et al., Nat Commun* **14**, 2062 (2023).
Barragán *et al., . Electrochimica Acta* **56**, 8630–8637 (2011).
Luo *et al., Energy Environ. Sci.* **14**, 4961–4978 (2021).

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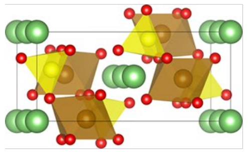
Conclusions & following of the project

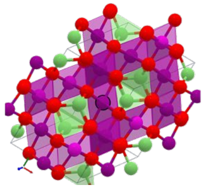
Electrochemistry for a circular economy

ELIP in cea

Materials



LFP vs. **LMO**

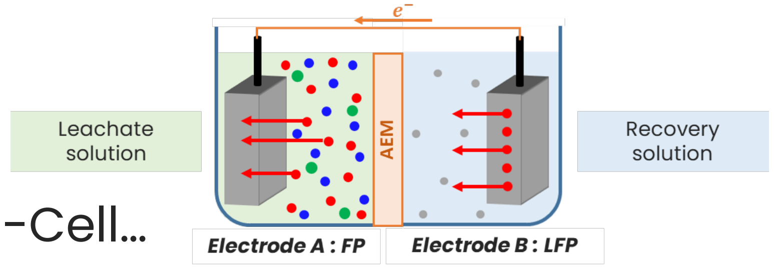


Both materials have good performances

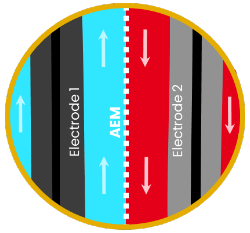
What about selectivity ?
What about durability ?
What about organic polluants ?

Technology

From a static H-Cell…

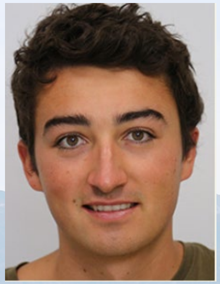


… to a Flow-Cell ?



Acknowledgements

Most of the work presented here was investigated by **Corentin Bourdiol**



In collaboration with

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cea liten

Thank you for your attention ☺

Questions ?

cnrs GDR Groupement de recherche

Prométhée Procédés hydrométallurgiques pour la gestion intégrée des ressources primaires et secondaires