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

High increase of the worldwide Electric Vehicle (EV) market

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

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)

Worldwide Battery Sales Forecasts (MWh) by Sector

>90% for EV

Electronic devices

Electric Vehicle (China excluded)

Electric Vehicle (China included)

Industry, energy storage

Other

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

<table>
<thead>
<tr>
<th>Recycling efficiency (%w)</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target 2027</td>
<td>65%</td>
<td>90%</td>
<td>90%</td>
<td>50%</td>
</tr>
<tr>
<td>Target 2031</td>
<td>70%</td>
<td>95%</td>
<td>95%</td>
<td>80%</td>
</tr>
</tbody>
</table>

Li is now considered as a critical material

2030 : 350 millions electric vehicle will have been produced

Li is now considered as a critical material

Environmental, economical and geopolitical concerns

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

Avicenne Energy, 2021

International Energy Agency, 2022

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

- **Solvant extraction**
  - Organics use
  - Expensive

- **Precipitation**
  - Low selectivity

- **Electrodialysis**
  - Low capacity and durability

- **Nanofiltration**
  - Low capacity and durability

- **Absorption**
  - Low capacity

- **Electrochemical Li Ion Pumping (ELIP)**
  - Selective
  - Low costs
  - Few reagents

Focus: Study of ELIP process

References:
- Xu, Ping et al, Journal of Material Science, 2020
- Pasta, Battistel, Mantia, Energy Environ. Sciens 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*

- **Li insertion**
- **Solution exchange**
- **Li deinsertion**
- **Counter electrodes**
- **Insertion material**

**Goal:** Use ELIP for battery recycling
Material choice for ELIP process

All possible insertion materials

Li selectivity

Filter

Knowledge

Water stability

Cost

LFP

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

LFP : LiFePO₄

Olivine structure along the zone axis [010]

Study of LFP as the insertion material
Electrode production:

Coating synthesis method

Active material: $\text{LiFePO}_4$
+ $e^-$ conductor: $\text{C Super P}$
+ Binder: $\text{PVDF}$
+ Solvant: $\text{NMP}$

Selected substrate: carbon cloth

3-Electrodes set up:

WE: Working Electrode
CE: Counter Electrode: Platinium grid
Ref: Ag/AgCl with saturated KCl reference electrode
Selected electrolyte: $\text{LiNO}_3 \ 0.5M$
Experimental – 3 electrodes setup

Microscopic characterization:

MEB and HRTEM images of LFP powder

MEB image: cross-section of LFP onto CC electrode
These electrodes are sufficient for conducting more in-depth studies.

Study of capacity

Initial capacity ~150 mAh/g
Reproducibility: OK
Durability: OK

\( WE \) capacities as a function of cycling

- Initial capacity ~150 mAh/g
- Reproducibility: OK
- Durability: OK

(\( WE \) capacities as a function of cycling)

- **Initial capacity ~150 mAh/g**
- **Reproducibility:** OK
- **Durability:** OK

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Experimental – 3 electrodes setup

Study of selectivity

Normalized E-I curves of delithied LFP in different electrolyte

<table>
<thead>
<tr>
<th>C-rate C/2</th>
<th>Capacity mAh/g</th>
<th>Ion radius Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃ 0.5M</td>
<td>150 ± 5</td>
<td>0.9</td>
</tr>
<tr>
<td>NaNO₃ 0.5M</td>
<td>110 ± 10</td>
<td>1.16</td>
</tr>
<tr>
<td>KNO₃ 0.5M</td>
<td>7 ± 3</td>
<td>1.52</td>
</tr>
</tbody>
</table>

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

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

- **Li vs Na**
  - 3C: 98.3 % ±1
  - C: 98.7 % ±0.5
  - C/10: 99.5 % ±0.1

- **Li vs K**
  - C/2: ~100

Good selectivity with K and Na, can be optimized

Coin cell production

Manufacturing protocols for coin cells

→ Working Electrode of interest : LFP

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

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

→ 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

Good stability of the electrodes in aqueous electrolyte

Objective: understanding degradation mechanisms

Nyquist graph evolution of a PB during 1C cycling

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

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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

Ongoing studies:

→ Understand degradation mechanisms
  *Coupling electrochemical characterisation with HRTEM, EELS, DRX, PEIS*

→ Electrode performance (in complex electrolytes)

→ Final goal: find the right balance

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Speed   Capacity
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Stability   Selectivity
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Thanks