Electrochemical lithium recovery as a greener and selective approach for Li-ion batteries waste treatment

B. Marin(bmarin@leitat.org), A.M. Escamilla, C. Aucher Leitat, (Energy Storage), 08225 Terrassa, Spain.

Introduction

The demand for lithium has surged due to its crucial role in lithium-ion batteries, which power electric vehicles (EVs), portable electronics, and energy storage systems. The global lithium market is expected to grow driven by the expansion of the EV market and energy storage systems. Driven by this scenario, the primary objective of BATRAW (HORIZON EUROPE GA 101058359) is to develop and demonstrate an efficient pre-treatment and continuous hydrometallurgical recycling of battery cells and modules.

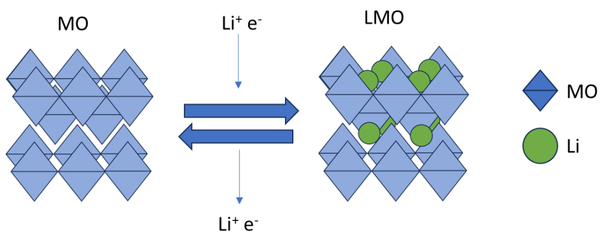
Traditional lithium extraction methods, such as mining and evaporation ponds, are resource-intensive and environmentally detrimental. LEITAT proposes the implementation of innovative technologies such as electrochemical lithium recovery (ELR). This approach leverages electrochemical principles to selectively extract lithium ions from various sources, including brine, seawater, and recycled battery materials. The system typically comprises an electrochemical cell with specialized electrodes designed to capture lithium ions efficiently.

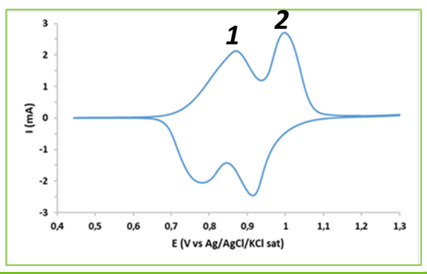
ELR Concept

In ELR a host structure, **generally transition metal oxides, can capture and release lithium ions by applying or receiving a current**. An oxidation change occurs in the transition metal present in the structure, allowing the insertion and disinsertion of lithium ions[1].

1) $2\lambda - Mn_2{}^{IV}O_4 + 0,5Li^+ + 0,5e^- \rightarrow Li_{0,5}Mn_{0,5}{}^{III}Mn_{1,5}{}^{IV}O_4 \;\; E^o = 0,74V$

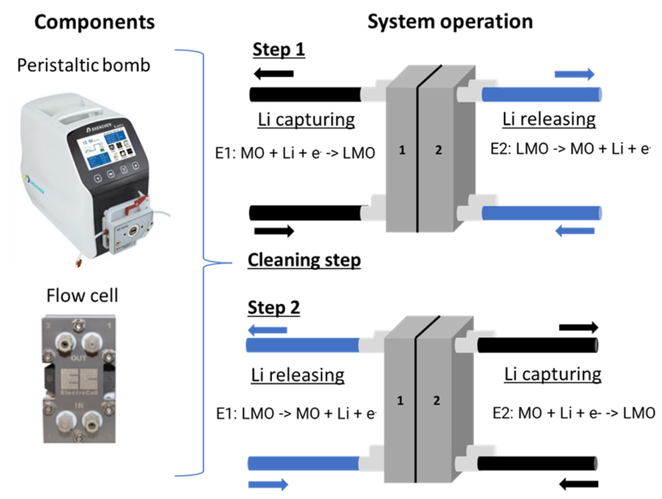
2) $Li_{0,5}Mn_{0,5}{}^{III}Mn_{1,5}{}^{IV}O_4 + 0,5Li^+ + 0,5e^- \rightarrow LiMn^{III}Mn^{IV}O_4 \;\; E^o = 0,85V$





https://doi.org/10.1016/j.elecom.2021.106980

Flow System Concept



This cell is composed of two chambers separated by an anion exchange membrane (AEM).

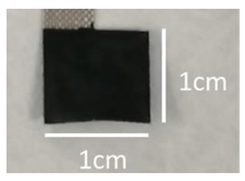
In each chamber an LMO electrode is inserted allowing the lithium capture/release while the opposite reaction is been conducted in the opposite chamber.

Once the process is finished, the liquid is extracted and exchanged for the one used in the other chamber.

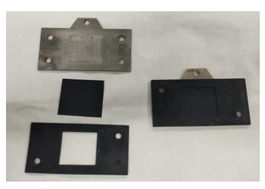
Experimental

Electrode configuration

Ink formulation: 80/10/10 : LMO, Super P and PVDF
Batch electrode: Coated on a 1 x 1 cm Stainless Steel mesh.
Flow electrode: Coated on Aluminium foil. The foil is stick to a Ti plate using a viton gasket.



Batch electrode

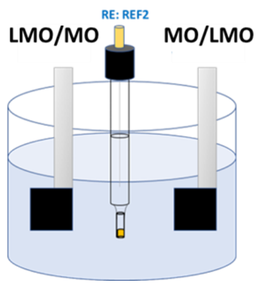


Flow electrode

Batch to batch system

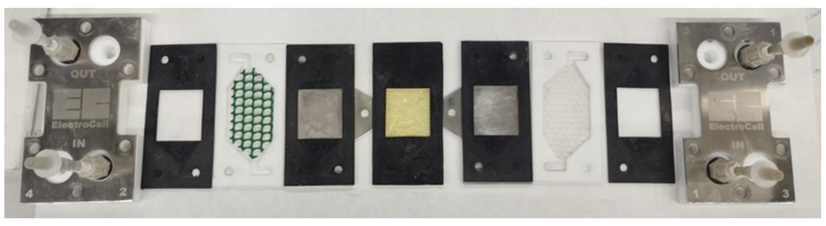
Cyclic Voltammetry: 0.1mV/s from 0.4 to 1.3V.
Charge-discharge: CC charge/CC discharge from 0.4 to 1.3V **(1C for Li concentration test and 2C for cyclability test).**

Electrolytes:
pH: Li_2SO_4 1M pH: 3, 5, 9, 12.
Presence of impurities: MSO_4; M=Na, K, Co, Mn and Ni.
Li concentration: Li_2SO_4; [Li]: 0.5, 1, 1.5, 2, 2.5M.
Ciclability: Li_2SO_4 1M.



Three-electrode symmetrical system using:
WE: LMO/MO
CE: LMO/MO
RE: Ag/AgCl/KCl sat

Flow system



1 2 3 4 5 4 3 2 1

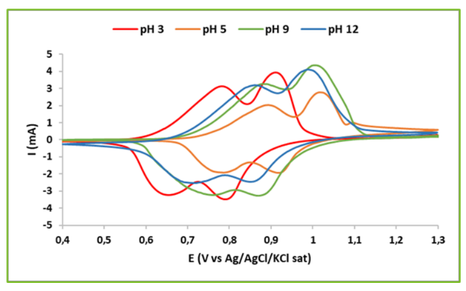
1)Polypropylene (PP) frame
2) Vinton gasket.
3) PP frame with a turbulence mesh.
4) LMO flow electrodes
5) Anion Exchange Membrane (AEM) sandwiched between two Viton gaskets.

Charge-discharge: 2C CCCV charge/CCCV discharge from -0.8 to 1.5V for 15 charge/discharge cycles. **(Flow Rate: 10mL/min).**
Recovery electrolyte: 0.1M Li_2SO_4.
Model liquor: 1M Li_2SO_4.
ICP-MS: An aliquot is taken every 5 charge/discharge cycles for analysis.

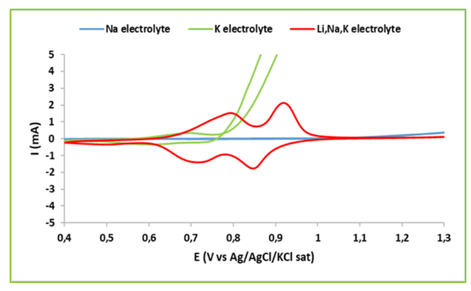
Results

Batch to batch system

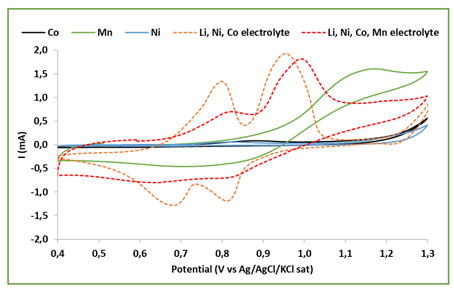
ph



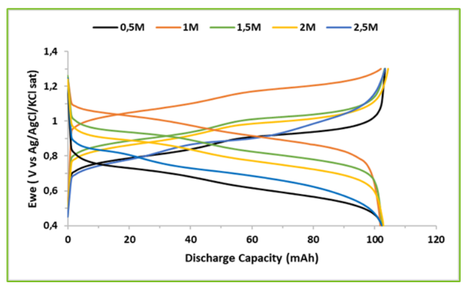
Presence of impurities I. Monoatomic cations



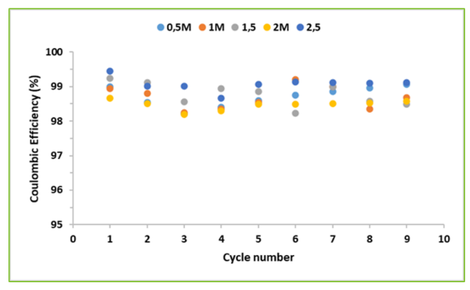
Presence of impurities II. Transition metals



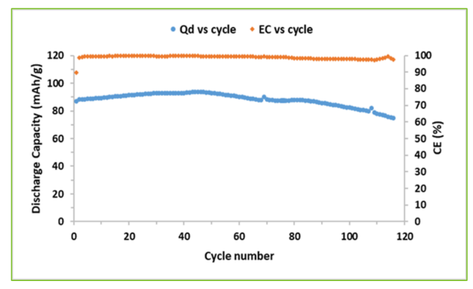
Li concentration I



Li concentration II



Ciclability

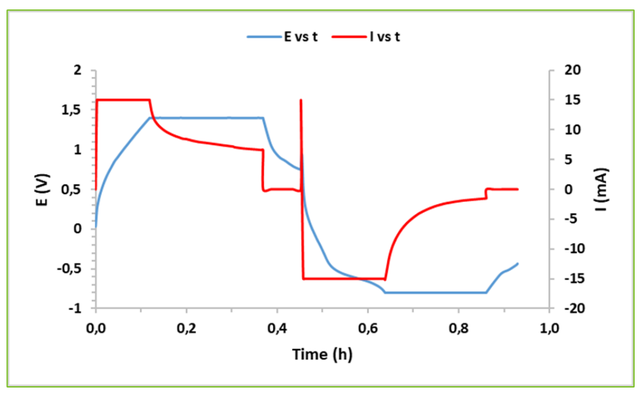


Batch to batch System highlighted results

1) LMO can work in a wide ph window **from 3 to 12.**
2) LMO shows a **great selectivity for Li** in presence of another monovalent cations (**Na^+ and K^+**) however the presence of **Mn** could lead to a **capacity loss** because it produces a reaction with LMO.
3) Li concentration does not affect the lithium insertion and **disinsertion ([Li]= 0.5 - 2.5M).** In fact, LMO shows a great **coulombic efficiency (99%)** during charge discharge tests.
4) A high cyclability of **120 cycles** is observed while charging/discharging at 2C.

Flow system

Charge-discharge-Flow



ICP-Flow

Sample code	Li mg/Li	ΔLi mg/L	ΔLi mg/ cycle	Q mg/g LMO	W_{charge} Wh/ mol	$W_{discharge}$ Wh/ mol	W_{system} Wh/ mol
[Li] 0	1310						
[Li] 1	1370	60	6.0	25.2	10.4	-4.0	6.3
[Li] 2	1438	68	6.8	28.3	9.2	-3.6	5.6
[Li] 3	1494	56	5.6	23.1	11.3	-4.4	6.9
Average results		61	6.1	25.5	10.3	-4.0	6.3

Conclusion

Electrochemical approach is a viable alternative for lithium recovery, with benefits such as excellent lithium selectivity, short reaction times, and low energy consumption. In this work, a symmetric LMO/MO system was studied in a batch-to-batch system and in a flow system. The effect of different parameters such as pH, Li concentration, Li selectivity and current applied were evaluated and optimized in a batch system. It was observed that the system can work in a wide pH window (3-12) while showing high selectivity for lithium ions in presence of other monovalent ions (*e.g.* Na^+ and K^+). Besides, lithium concentration does not affect the recovery rate. Regarding the electrochemical performance, LMO exhibit a capacity around 90 mAh/g for 120 cycles under a 2C current. Final tests were performed in a flow system exhibiting an extraction capacity of 25.5 mg of Li per gramme of LMO with an energy consumption of 6.3 kWh/mol of lithium recovered.

Co-funded by the European Union

UK Research and Innovation

This project has received funding from the European Union's Horizon Europe research and innovation programme under grants agreement No 101058359. Isle Utilities Ltd participant in Horizon Europe Project BATRAW is supported by UKRI.