XLII Reunión del Grupo Especializado de Electroquímica
de la RSEQ (42 GERSEQ 2022) - Santander, 6-8 Julio 2022
Defensa del Plan de Investigación

Electrochemical lithium recovery using 3D faradaic electrodes based on graphite felt

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Santander, Spain – July 6th, 2022

Motivation: lithium supply vs demand

Key Lithium Applications[1]:


Li-Ion Batteries – Portable Devices


Li-Ion Batteries – Electric Vehicles


Glass & Ceramics


Energy storage


Grease


Aluminium-alloys


Pharmaceuticals

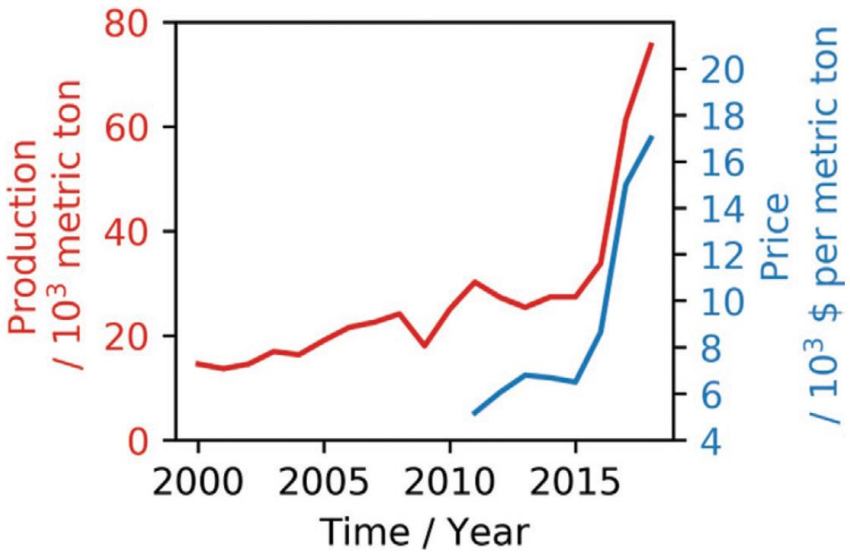


Figure 1. Production and price of lithium[2].

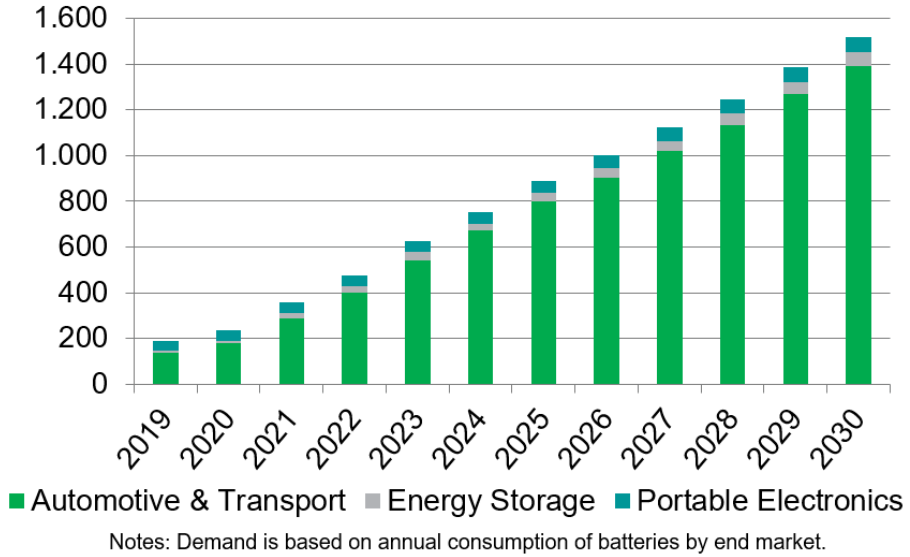
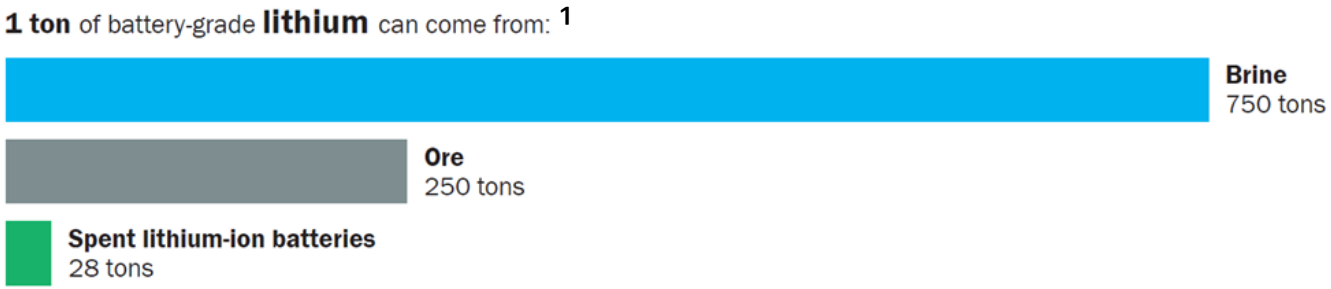


Figure 2. Global battery demand by major end market (GWh)[3].

Until 2025 [4]:
LIBs and other industries will consume up to 140 x 10^3 tons of lithium

[1] Eramet Alloys, Ores and People, Investor presentation, 2017. [2] Battistel *et al.* Adv. Mater. 32 (2020) 1905440.
[3] IHS Markit; images left are from Getty Images and Shutterstock, 2020. [4] Zhou et al. J. Energy Chem. 59 (2021) 431–445.

Lithium extraction from brine



- South America: largest lithium containing brines (80%) are in salt flat (65% of the world reserves)[2]:
  - "Lithium Triangle": the largest and highest quality lithium brine deposits;
  - Salt flats at 4000 meters above sea level.

- Currently most extended lithium extraction method from salt flat brine[2]: lime-soda evaporation process
  - very slow (8-12 months evaporation);
  - dependence on weather conditions;
  - chemicals added (lime, solvay);
  - waste generation ($CaSO_4$, NaCl, $Mg(OH)_2$);
  - water loss (millions of gallons per ton).

[1] FCAB, National Blueprint Lithium Batteries 2021–2030, 2021. [2] Calvo, Nanotechnology for energy storage and sustainable extraction of lithium from natural brine, Nanomercosur, 2017. [3] Battistel *et al.* Adv. Mater. 32 (2020) 1905440.

Electrochemical Lithium Ion Pumping

Fast
Environmentally friendly
Low energy cost
Highly selective for lithium

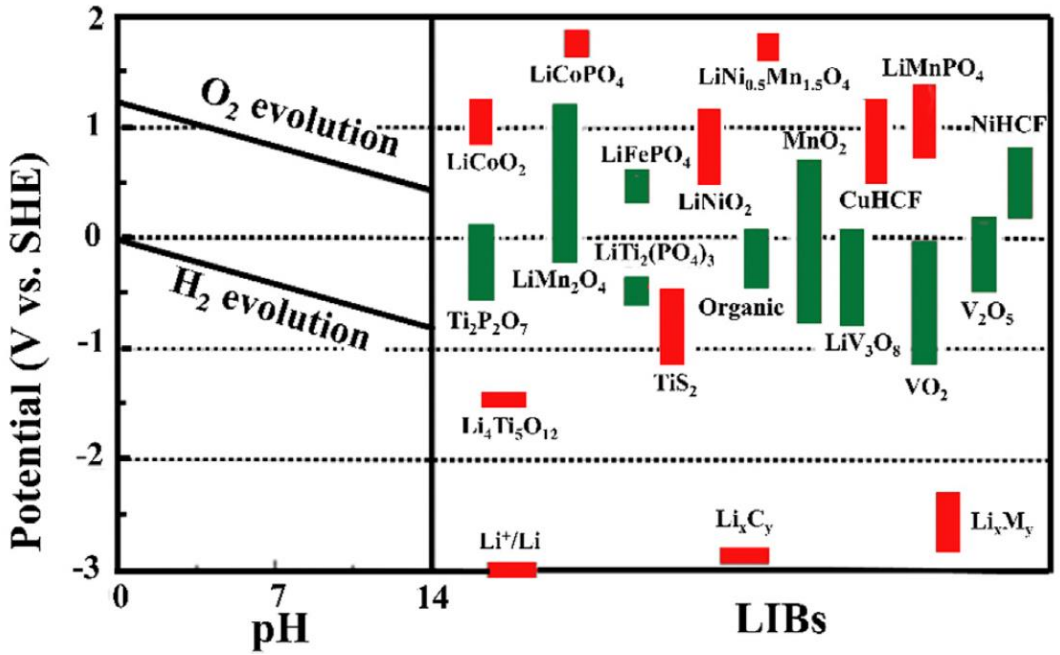


Figure 3. Electrochemical stability potential of water and redox potentials of electrode materials used in lithium-ion batteries.[1]

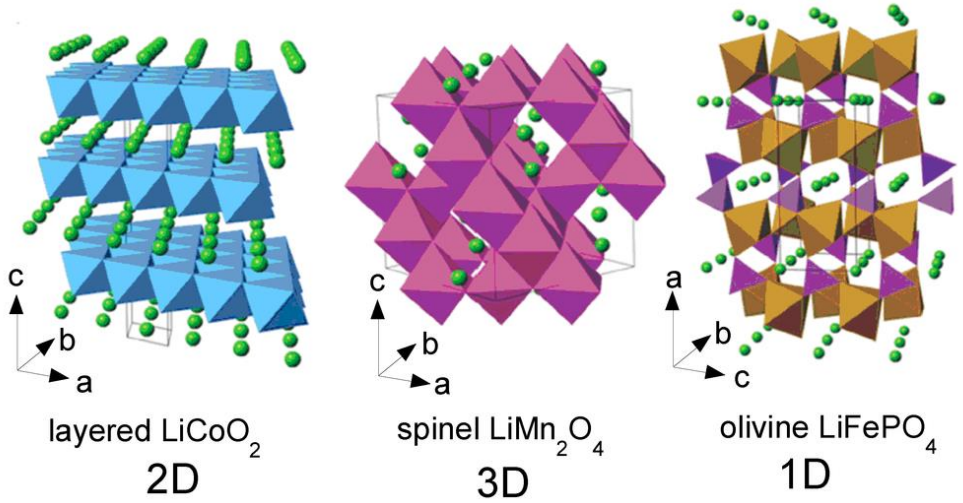


Figure 4. Dimensionality of the Li+ ions transport.[2]

- **Du et al. (2016)[3]**: Selective lithium extraction using nanoscale λ-MnO_2/PPy/PSS core-shell rods: 35.2 mg g^{-1}, equilibrium time < 2 h.
- **Mu et al. (2021)[4]**: mesoporous λ-MnO_2/$LiMn_2O_4$ modified 3D graphite felt electrodes: 26.1 mg g^{-1}; high stability (90% in 20 cycles), fast mass transfer kinetics (75 mg_{Li+} h^{-1} g_{LMO}^{-1}) and high Li/Mg separation coefficient (46).

[1] Kim *et al*., Chem. Rev. 114 (2014) 11788–11827. [2] Julien *et al*. Inorganics 2 (2014), 132-154.
[3] Du *et al.* J. Mater. Chem. A. 4 (2016) 13989–13996. [4] Mu *et al.* Desalination. 511 (2021) 115112.

Electrochemical Lithium Ion Pumping

$$2\lambda\text{-}MnO_2 + 0.5\ Li^+ + 0.5\ e^- \leftrightarrow Li_{0.5}Mn_2O_4$$

$$Li_{0.5}Mn_2O_4 + 0.5\ Li^+ + 0.5\ e^- \leftrightarrow LiMn_2O_4$$

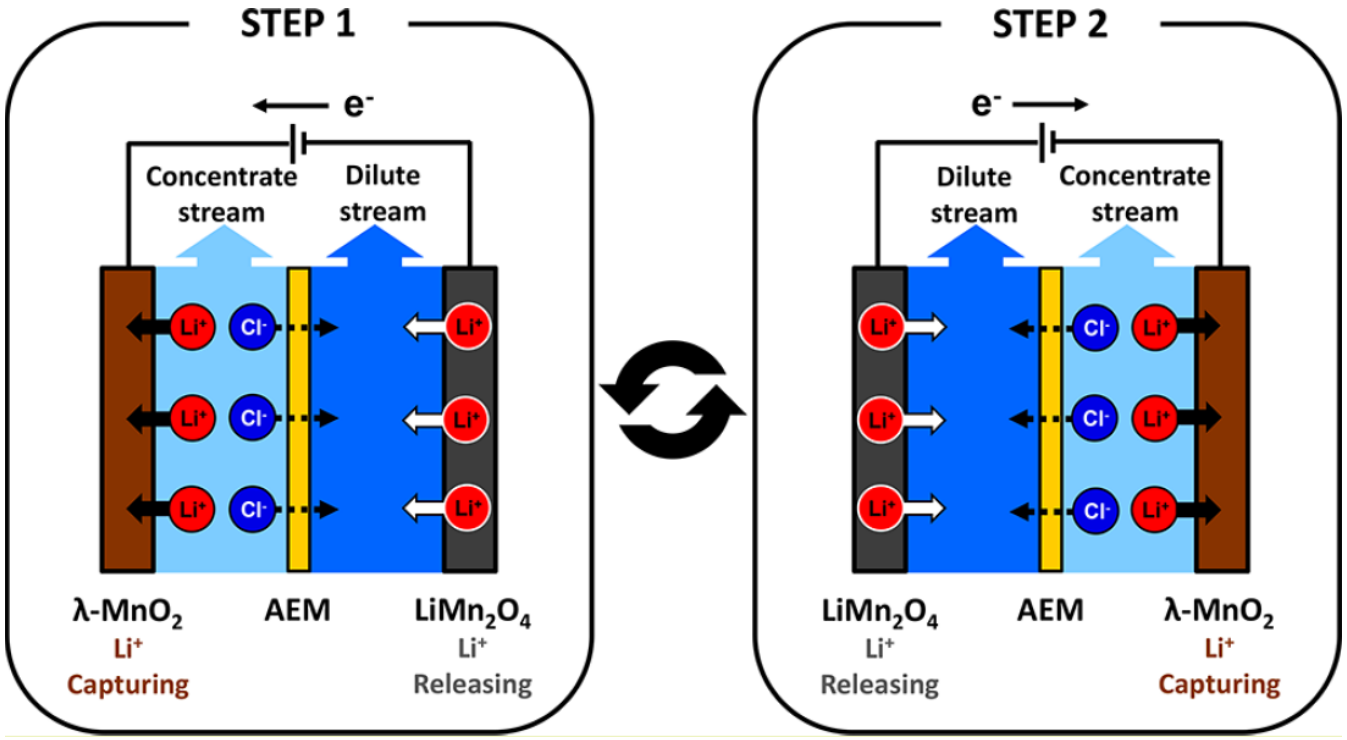


Figure 5. Representation of the λ-MnO_2/$LiMn_2O_4$ system for lithium recovery using a rocking-chair cell.[1]

[1] Joo *et al.*, ACS Sustain. Chem. Eng. 8 (2020) 9622–9631.

Challenges:

- Development of electrode materials with:
  - High Li^+ removal capacity;
  - Fast intercalation/desintercalation kinetics;
  - Low cost;
  - Scalable in production;
  - High stability;
  - Li^+ selective;
  - Long useful life.
- Understanding and optimizing the process operating conditions

Objectives

To study the performance of faradaic materials supported on graphite felt as stable, low cost and high performance 3D electrodes in electrochemical lithium recovery.

- Optimize the electrode preparation method: homogeneous and well-adhered film;
- Understand the influence of structural/textural properties of the electrodes on lithium capture capacity;
- Understand their electrochemical properties on kinetics, charge efficiency and energy consumption;
- Carry out the proof of concept of the 3D rocking chair cell for lithium recovery: proper functioning of the system (hydraulic and electrochemical level);
- Pre-optimize operating conditions (electrical and fluid dynamics) for lithium recovery;
- Evaluate the performance of the electrodes in the electrochemical lithium recovery using the continuous flow rocking chair cell, in media with different concentrations of lithium;
- Assess the electrochemical stability of the electrodes during long-term deionization;
- Study the electrode selectivity in a multi-ion solution (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, etc).

Electrochemical lithium recovery using 3D faradaic electrodes based on graphite felt

Electrode

Preparation

- Immersion time
- Ink density (mg_{LMO}/mL_{isopr})

Characterization

Structural

- **TEM, SEM-EDX** (morphology)
- **XDR** (crystalline structure of spinel LMO)
- **FTIR** (groups by chemical bonds = Mn-OH, Mn-O-Mn, etc)
- **Raman/XDR/FTIR** (changes after several cycles)
- **Wettability** (hydrophilicity)

Electrochemical

3 electrodes cell

- **CV** (redox reactions)
- **GCD** (charge storage capacity and ohmic drop)
- **EIS** (R_Ω, R_{CT}, E_{PZC})
- **GITT** - Galvanostatic Intermittent Titration Technique (Li^+ diffusion coefficient)

2 electrodes cell

Lithium Recovery

Proof of concept of the 3D rocking chair

cell assembly, hydraulic and electrical testing, charge/discharge experiments

Optimization of the deionization conditions

i_{app}, potential window, operational control (CC and CC+CV) and flow (pseudo-single-pass and bacth)

Electrochemical Lithium Recovery

3D electrode in a rocking-chair flow cell, at different concentrations (1,0; 0,1 y 0,05 mol L^{-1} LiCl)

Selectivity

Multi ion solution (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, etc)
Input: iapp, [ion]
Output: SAC, Q_E y η

Metrics

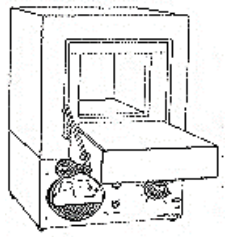
- **Capacity** (mAh g^{-1});
- **Salt adsorption capacity** (SAC, $mg_{sal}\ g_{electrode}^{-1}$);
- **Long-term stability** (capacity retention, %);
- **Charge efficiency** (Q_E, %);
- **Energy consumption** (η, kWh/mol)
- **Average (ASAR) and optimized (OSR) salt removal** ($mg_{sal}\ g_{electrode}^{-1}\ min^{-1}$)

3D electrode preparation

Graphite Felt (GF)[1]:
- 3D macrostructure
- high electrical conductivity
- easy scaling

GF thermal activation

Sigracell KFD
4.6 EA IW1



400 °C, 4h

OR

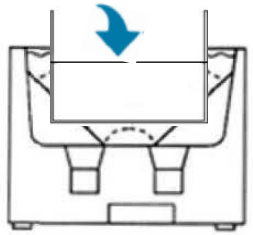
Commercial activated GF

Sigratherm GFD
4.65 EA IW1

80% **$LiMn_2O_4$ (LMO)** commercial +
10% CB

10% PVDF + isopropanol
(112 mg_{LMO}/mL_{isop})

Optimized



Ultrasonic bath

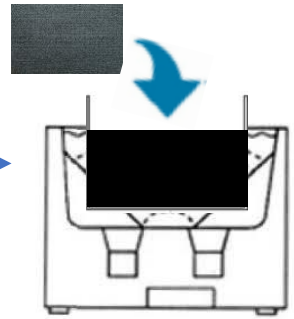
Homogenizer

High-energy ball milling
400 rpm, 30 min
Changing direction each 10 min

Homogenizer

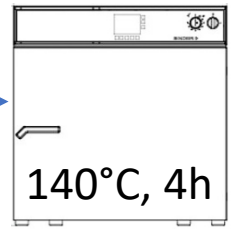
Optimized

Dip coating technique



Ultrasonic bath
(1 min submerged + 5 min drying + 1 min submerged)

Drying



140°C, 4h

[1] Wang *et al.*, Chem. Eng. J. 392 (2020) 1–11.

Experimental System

- **2-electrode cell:**
  - (+) and (-) electrodes (4.0 x 8.0 x 0.5 cm^3)
  - Anion-exchande membrane
- **Batch with recirculation[1]:**
  - Electrolyte volume: 50 mL (each tank)
  - Flow rate: 26 mL min^{-1}
- **Pseudo single-pass[2]:**
  - Electrolyte volume: 2 L
  - Flow rate: 10 mL min^{-1}

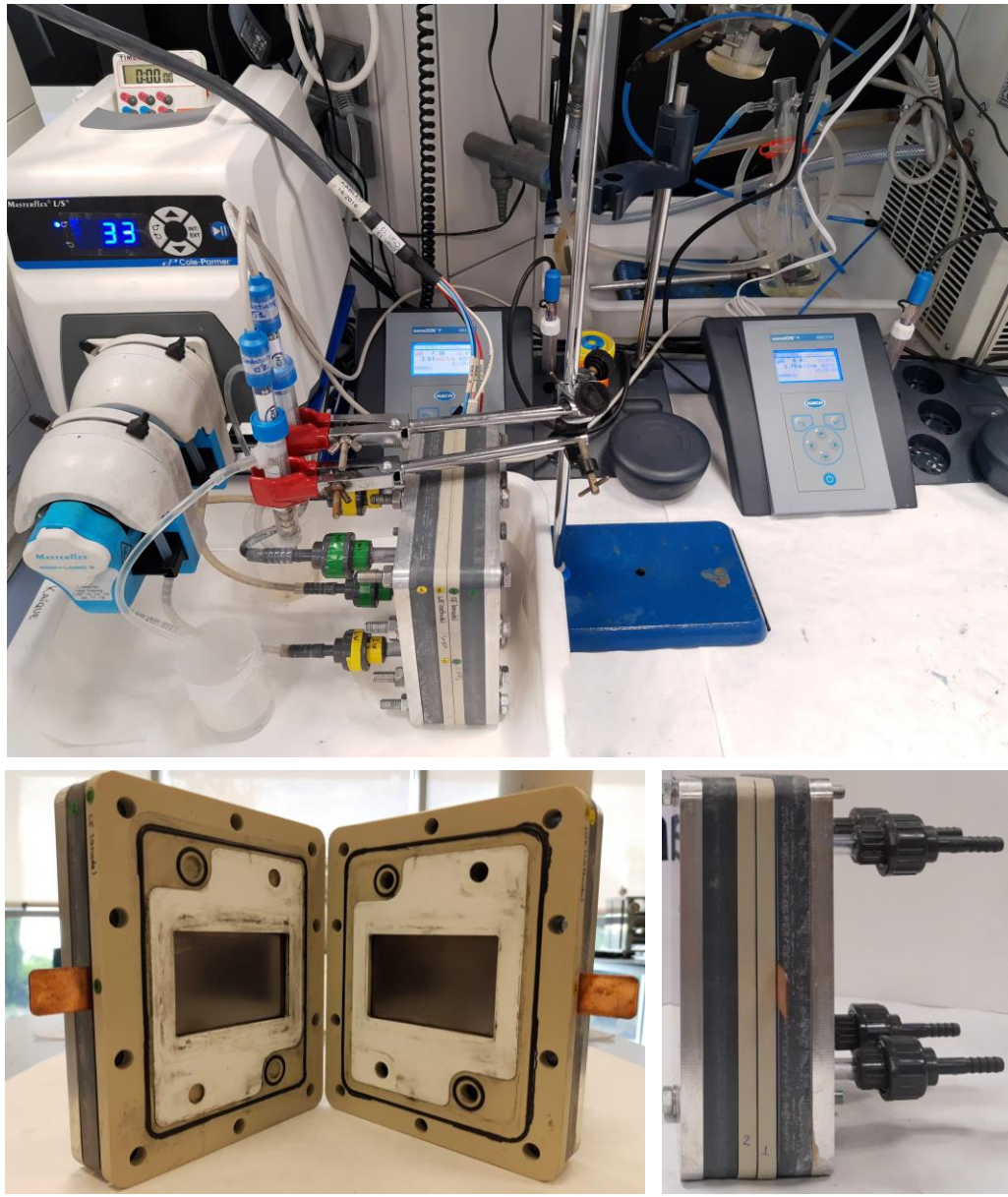


Figure 6. Photographs of the deionization system and 3D rocking chair cell.

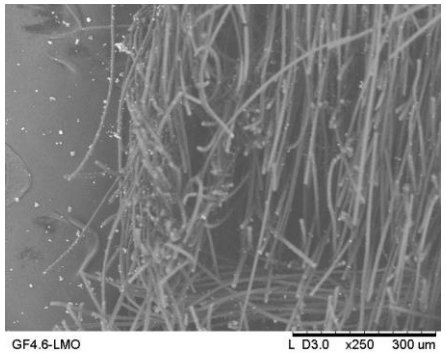
[1] Zornitta *et al.*, Carbon 156 (2020) 346e358. [2]Barcelos *et al.,* Desalination 492 (2020) 114594

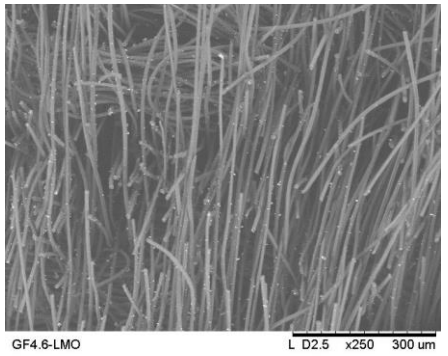
Structural characterizations

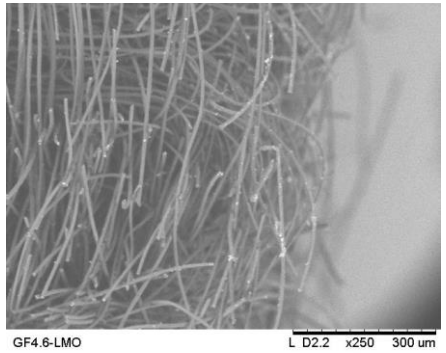
Optimizing the electrode preparation method

50.9 mg_{LMO}/mL_{isop} [1]
60 s + 5 s (drying) + 60 s

Mass loading = 3.3 mg_{LMO}/cm^2

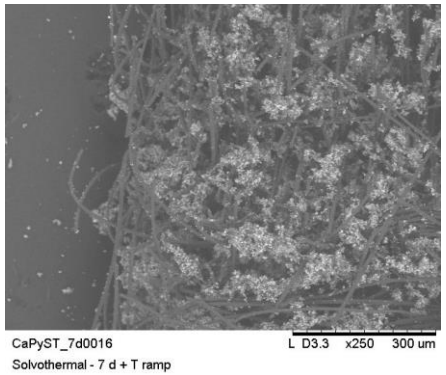


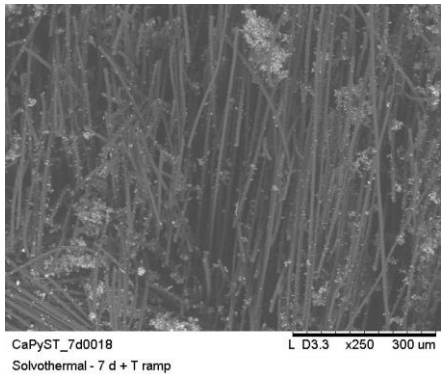


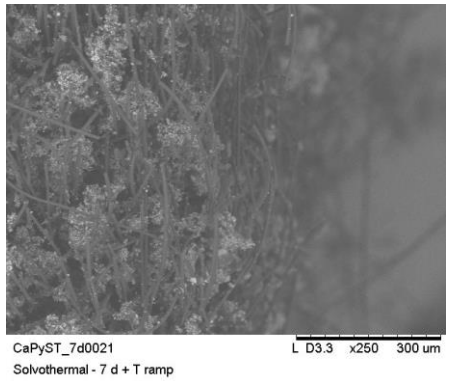


112.0 mg_{LMO}/mL_{isop} [2]
2 min + 1 min (drying) + 2 min

Mass loading = 40.0 mg_{LMO}/cm^2

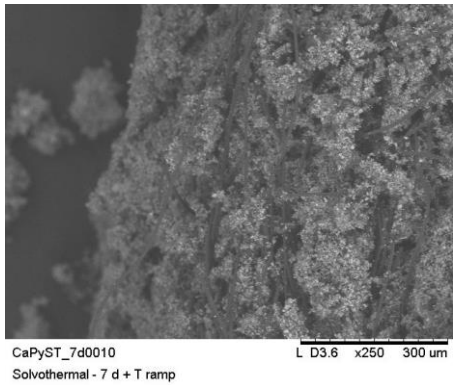


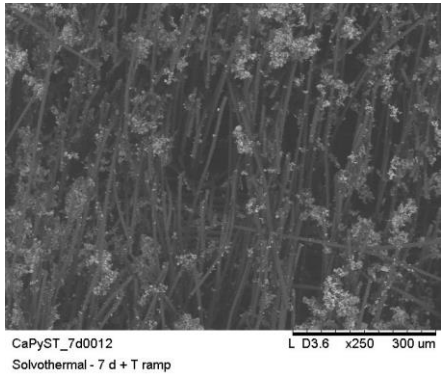


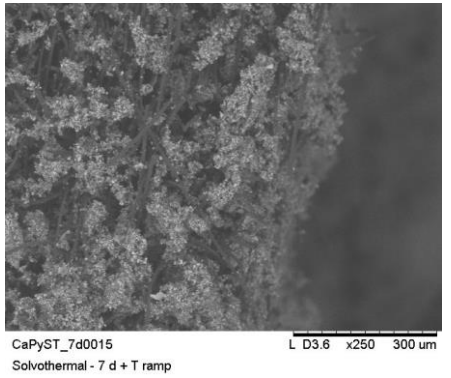


224.0 mg_{LMO}/mL_{isop}
2 min + 1 min (drying) + 2 min

Mass loading = 80.6 mg_{LMO}/cm^2



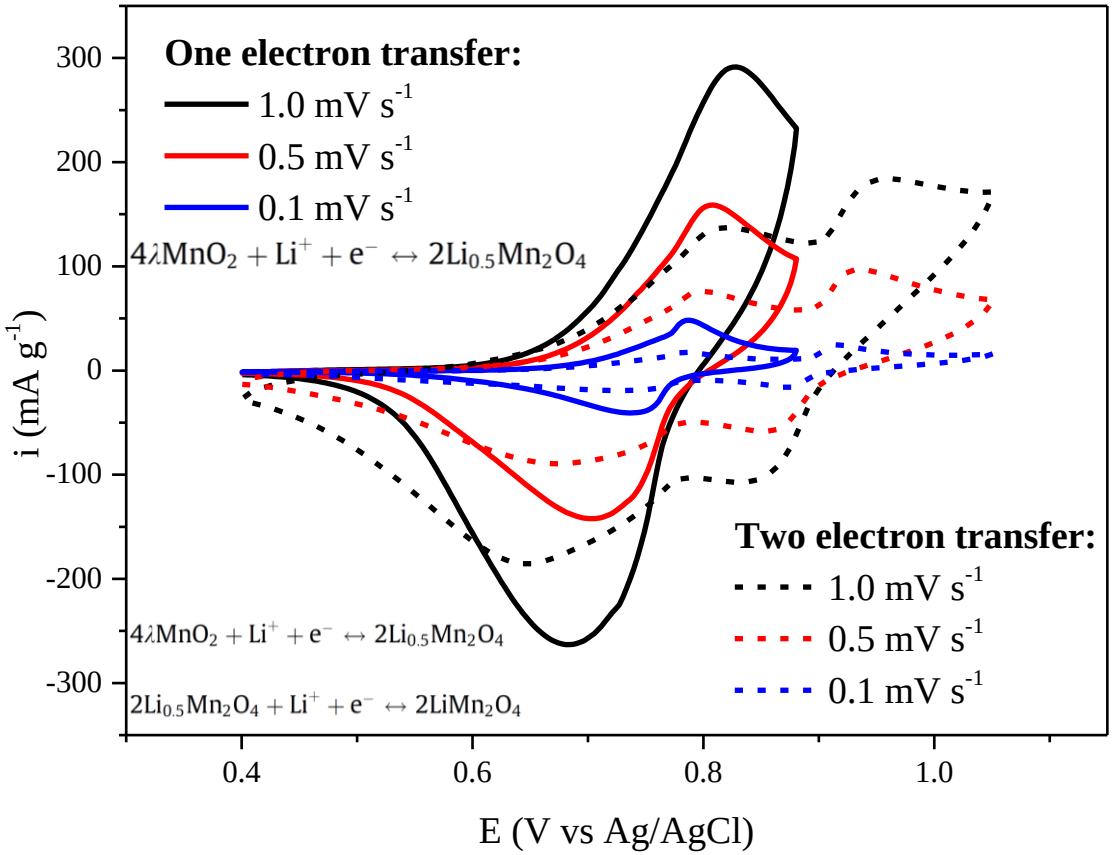


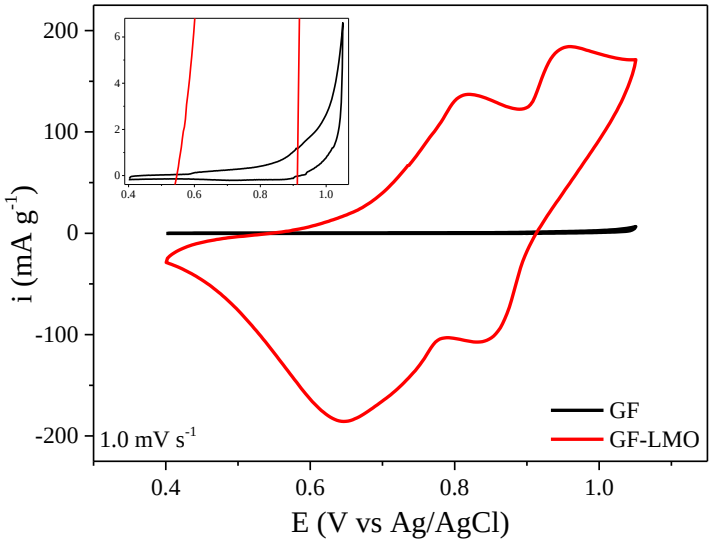


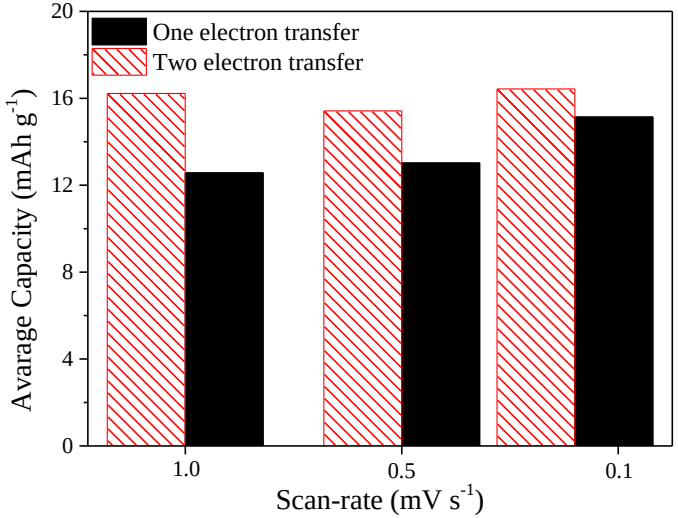
[1] Freire et al. *Separation and Purification Technology* 273 (2021) 118977. [2] Wang et al. *Chemical Engineering Journal* 392 (2020) 123698.

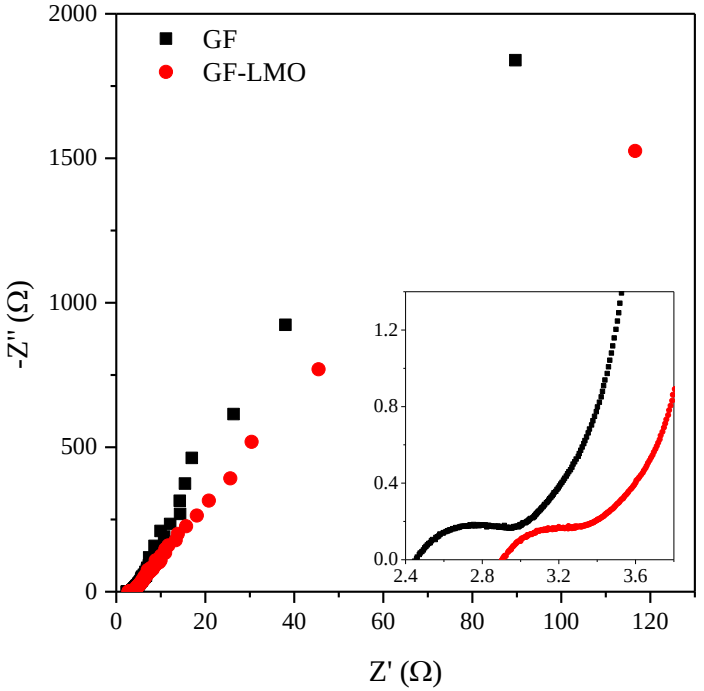
Electrochemical characterizations in 3 electrode cell

Becker with 3 electrodes
WE: GF or GF-LMO; **CE:** Pt;
RE: Ag/AgCl;
Electrolyte: 1 M LiCl







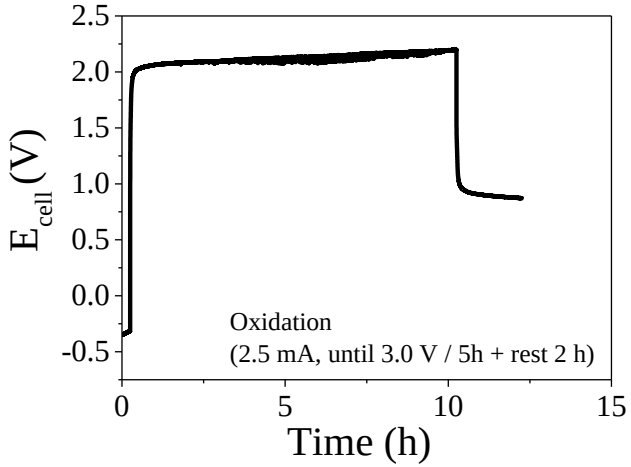


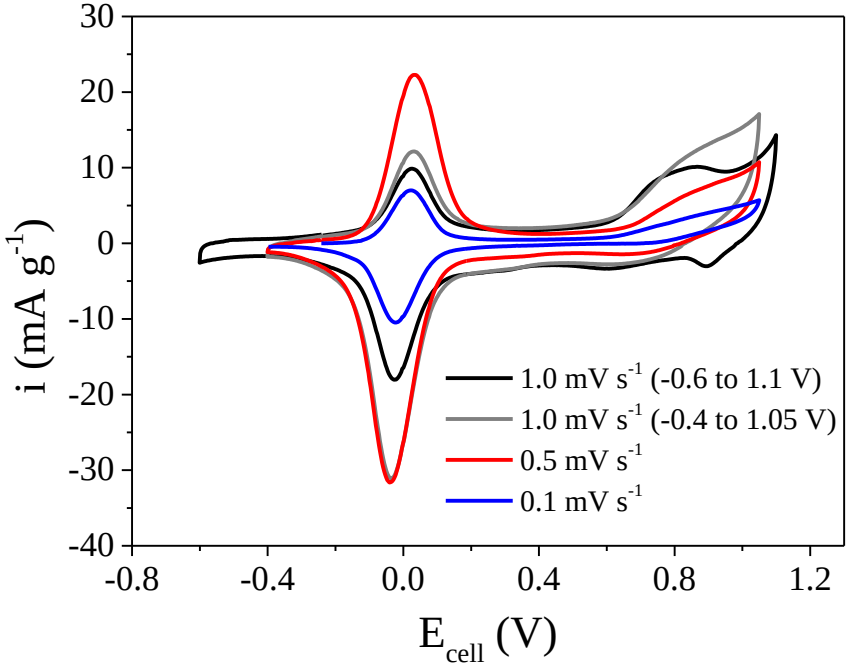
Circle fit	R_Ω (Ω)	R_{CT} (Ω)
GF	2.45	0.62
GF-LMO	2.91	0.57

$$Avarage\ capacity\ (mAh\ g^{-1}) = \frac{1}{2\,\nu\,m}\int_{E1}^{E2} I\,dV = \frac{1}{2\,m}\int_{t1}^{t2} I\,dt$$

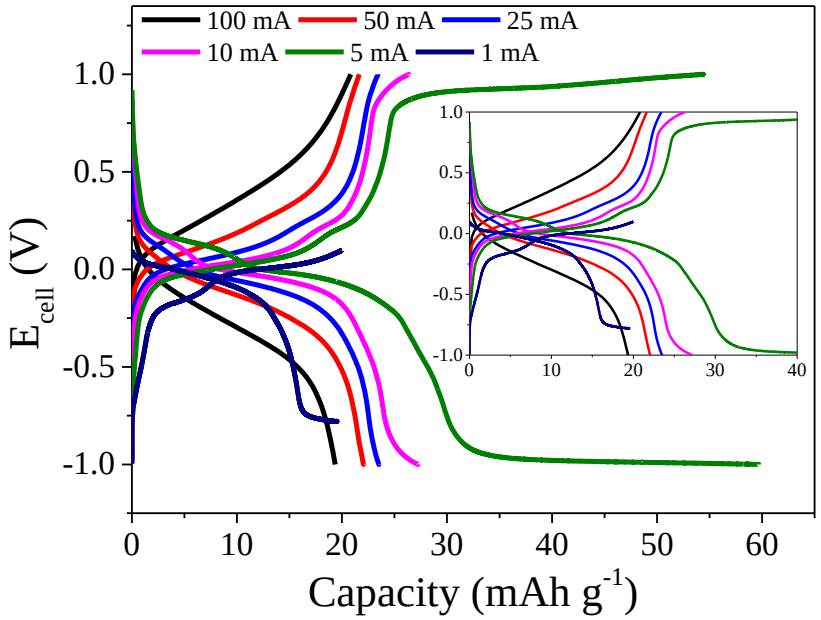
Electrochemical characterizations in 2 electrode cell

Cell with 2 electrodes
WE: GF-LMO; **CE:** GF-LMO;
Electrolyte: 1 M LiCl

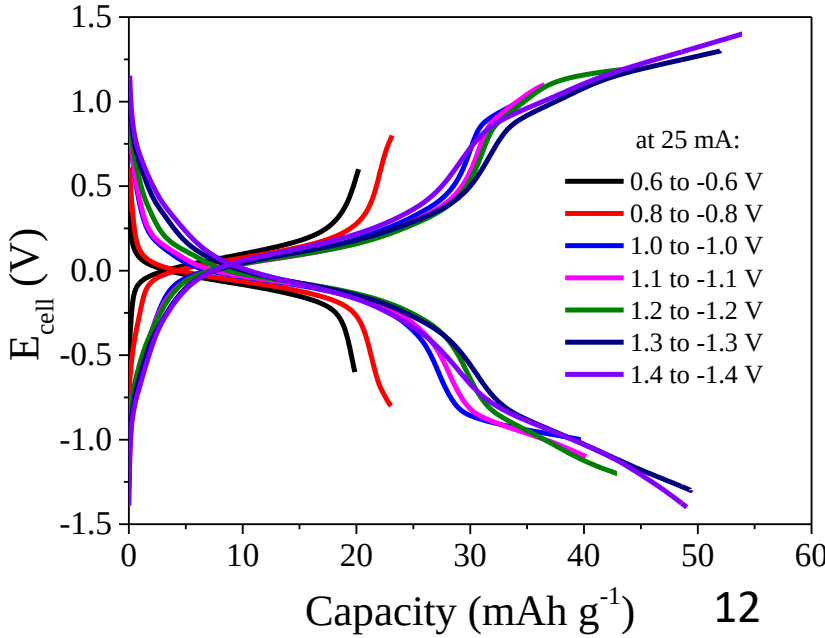




Evaluating the **applied current**



Evaluating the **potential window**

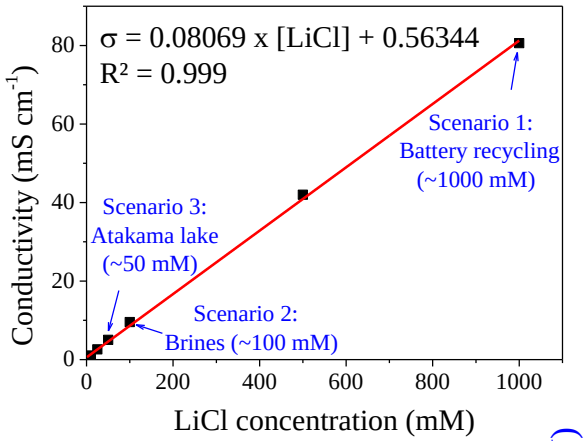


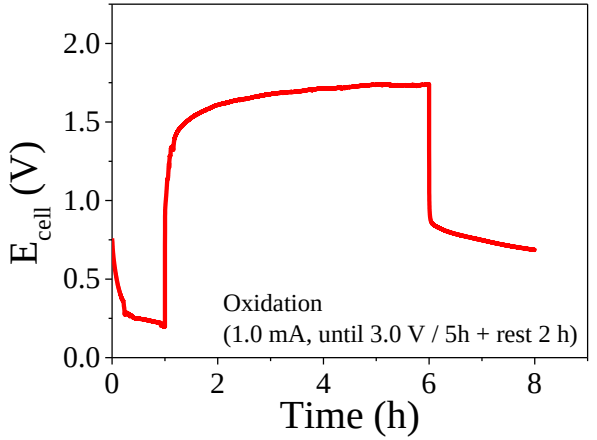
Lithium Recovery

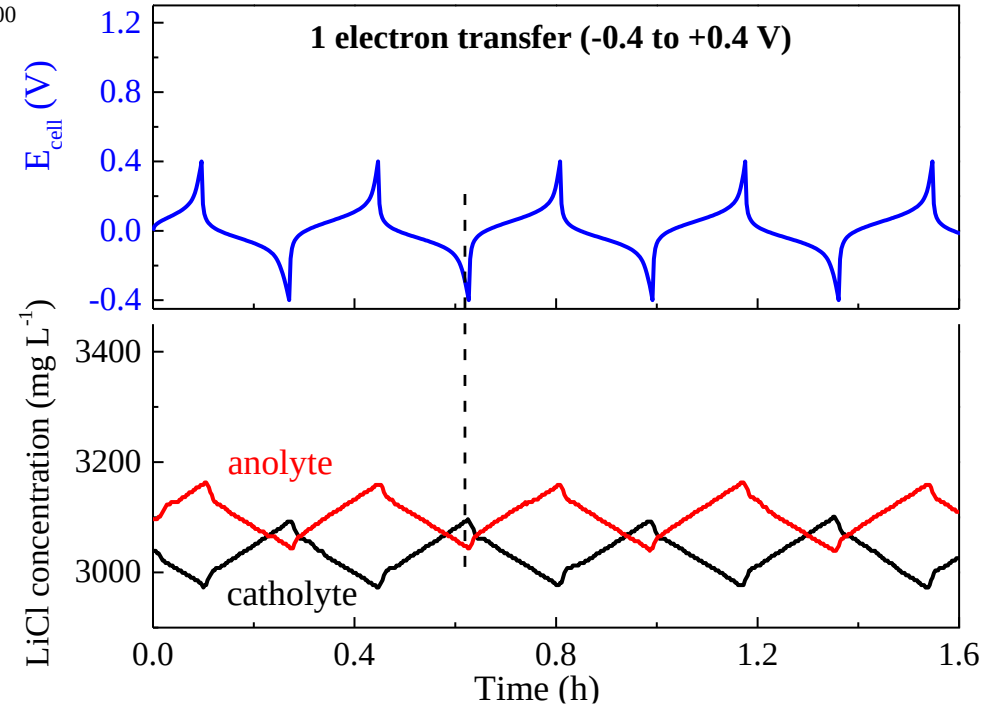
Conditions:

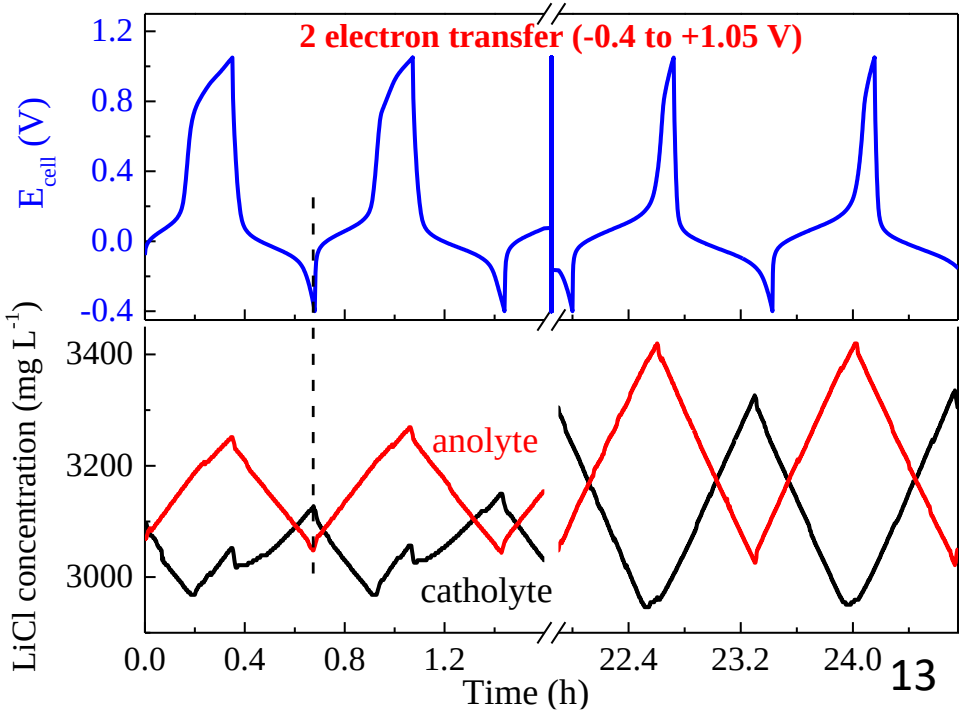
- **GF-LMO** (80% LMO: 10% CB: 10% PVDF) – (4.0 x 8.0 x 0.5 cm^3)
- **Batch**; q = 26 mL/min; V = 50 mL (each); [LiCl] = **0.1 M**; I_{app} = **25 mA**;
- **1 electron transfer**: -0.4<E_{cell}<0.4 V, **2 electron transfer**: -0.4<E_{cell}<1.05 V

Calibration curve

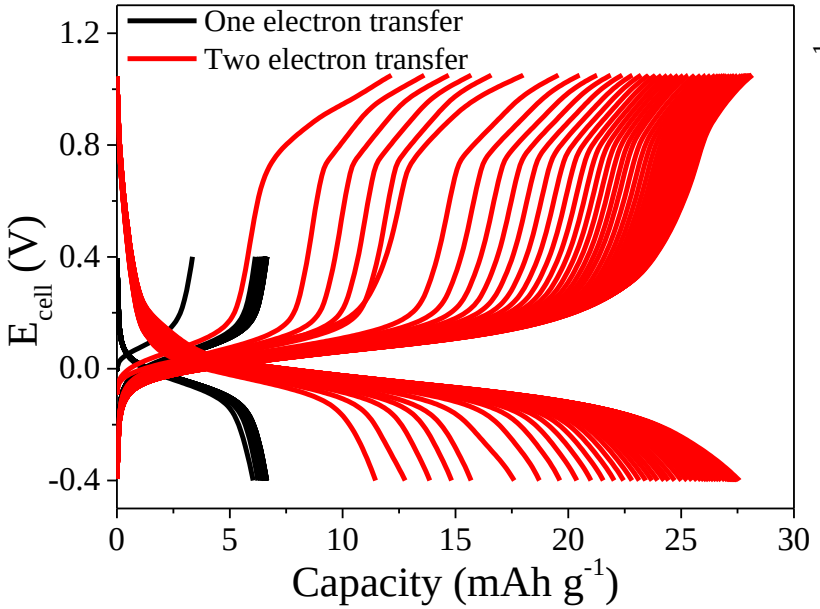


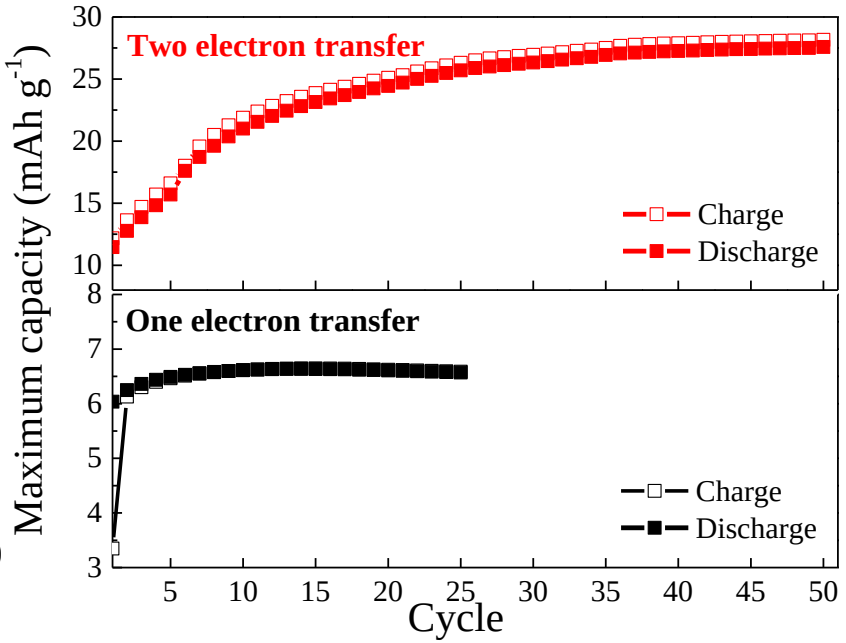


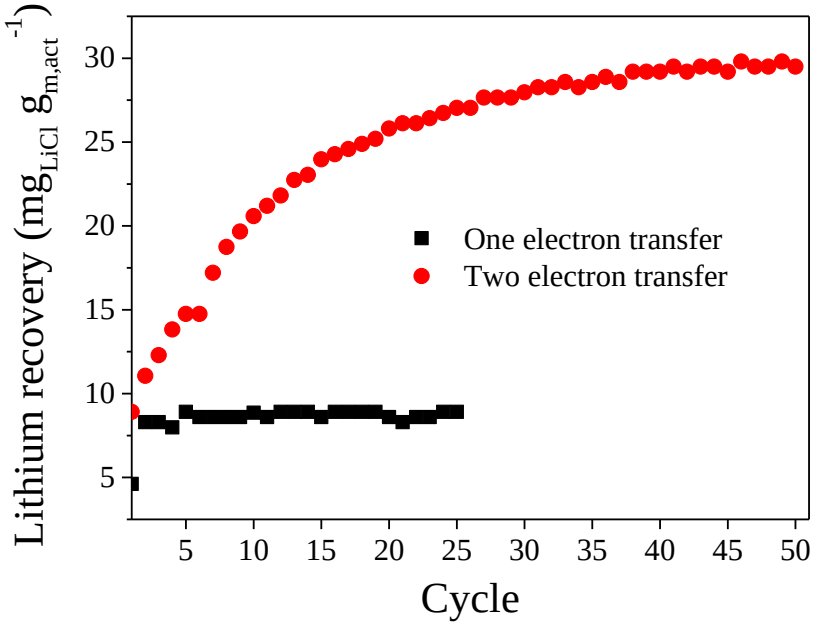




Lithium Recovery







[LiCl] (mol L^{-1})	Lithium recovery	SAC ($mg_{LiCl}/g_{m,act}$)
0.1	One electron transfer	8.7 ± 0.3
	Two electron transfer	29.4*
0.05	One electron transfer	0.19 ± 0.06
	Two electron transfer	8.76*
0.025	One electron transfer	1.82 ± 0.07
	Two electron transfer	1.82*

*Did not reach steady state. Parasitic reactions? This will be investigated.

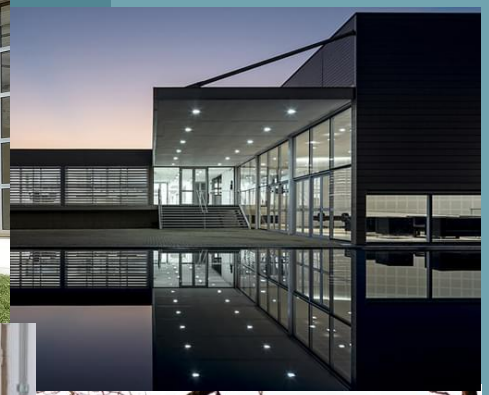
ACTIVITY SCHEDULE at UFSCar (Brazil) 1st to 5th semester (Mar. 2019 to Aug.2021)	YEAR / SEMESTER					
	2019/1	2019/2	2020/1	2020/2	2021/1	2021/2
Literature review and update	X	X	X	X	X	X
Mandatory and optional PhD subjects	X	X	X	X		
Defense of the Initial PhD Research Plan (02/29/2020)			X			
Capacitive deionization: activated carbon and electrode preparation (polyaniline modified with F127, lignin and banana peel), textural/electrochemical characterization, and desalination		X	X	X	X	
Faradaic deionization: preparation of faradaic materials and electrodes ($KNiFe(CN)_6$, $Na_2Ti_2O_4(OH)_2$, $H_2Ti_2O_4(OH)_2$, $Na_2Ti_2O_5$, $NaTiNbO_5$, $Na_4Nb(PO_4)_3$, $Na_xNb_y(PO_4)_3$@C), textural/electrochemical characterization, and deionization			X	X	X	X
Writing of scientific article (papers)			X	X		X
Defense of the Thesis Follow-Up Exam (10/29/2021)						X

Note: Schedule of proposed (dark blue) and completed (X) activities.

Note: Schedule of proposed (dark blue) and completed (X) activities.

ACTIVITY SCHEDULE	IMDEA Energy/ECyT UAM (Spain) Research Stay				UFSCar (Brazil)	
	Q1: Sep.2021 to Nov.2021	**Q2:** Dec.2021 to Feb.2022	**Q3:** Mar.2022 to May2022	**Q4:** Jun.2022 to Aug.2022	**Q1:** Sep.2022 to Nov.2022	**Q2:** Dec.2022 to Mar.2023
Literature review and update	X	X	X			
Thesis co-supervision agreement and ECyT/UAM registration	X	X				
Defense of the Research Plan (07/06/2022)						
Adaptation and training at IMDEA Energy	X					
Initial tests with intercalation materials for desalination and deionization	X	X				
Preparation and optimization of GF-LMO electrodes		X	X			
Structural and electrochemical characterization of GF and GF-LMO			X			
Proof of concept of the 3D rocking chair cell for lithium recovery			X			
Optimization of deionization conditions (i_{app}, potential window, operat. control and flow)			X			
Lithium recovery using GF-LMO electrodes in a rocking-chair flow cell, at different concentrations						
Selective intercalation using GF-LMO						
Extra: study of new electrodes for lithium recovery (LPF, redox polymers, etc.)						
Writing of scientific articles (paper, congress and thesis)						
Defense of the Thesis Qualification Exam (oct. 2022)						
Thesis Defense (until 02/28/23)						

Thank you!



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