Reusing and Recycling of Secondary Batteries

Juan Manuel Paz García
María Villén Guzmán
María del Mar Cerrillo González.

Department of Chemical Engineering – University of Malaga (Spain)

1ST / SESDIM
SUSTAINABLE ENERGY STORAGE DAYS IN MADRID
8th-11th OCTOBER 2019
Spanish National Research Council (CSIC) C/ Serrano, 117 - MADRID

UNIVERSIDAD DE MÁLAGA

Li-ion Batteries with Si Alloying Negative Electrodes

Silicon (**Si**) is a promising material to substitute/complement the C electrode

Advantages of Si:

- High gravimetric capacity (4200 mAh g^{-1})
- High volumetric capacity (9786 mAh cm^{-3})
- Low discharge potential (~ 0.4 V)
- Abundant
- Cheap
- Eco-friendly.

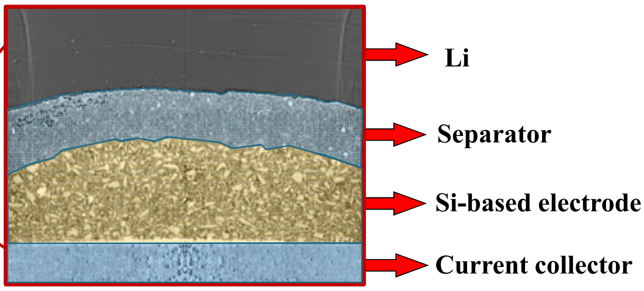
>12x graphite

$$\frac{4.4\ mol_{Li}}{mol_{Si}}\frac{mol_{Si}}{28\ g_{Si}}\frac{96485\ C}{mol_{Li}}\frac{mAh}{3.6\ C}\approx 4200\ mAh\ g^{-1}$$

juanma.paz@uma.es

UNIVERSIDAD DE MÁLAGA

LI-ION BATTERIES WITH SI ALLOYING NEGATIVE ELECTRODES



- Functional Li/Si cells
- X-ray transparent
- Nominal voltage 3.04 V

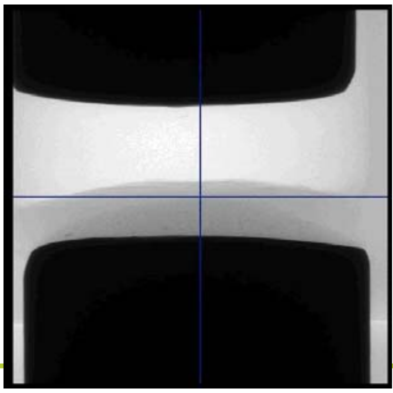
Electrode slurry contains (w%)
- 80% active material - **Si**
- 10% conductive carbon
- 10% PVDF

Computed Tomography

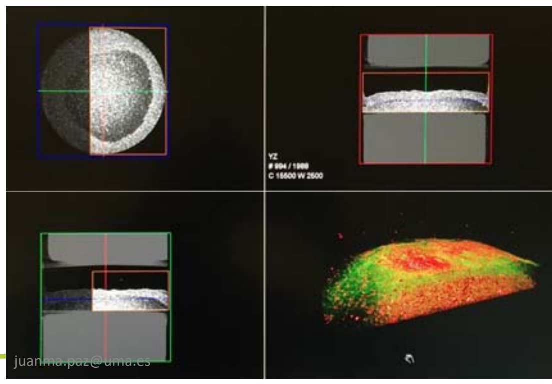
Parameters:

Sample X: -53 um Y: -26564 um Z: 52.5 um θ: -180.00 deg
Detector: 15 mm Source: -15 mm Filter: LE4
Voltage: 45.155kV Power: 3.5W
FOV: 3429.2 um, 3429.2 um Pixel Size: 1.6876
Obj: 4X Binning: 1 Exposure: 30s

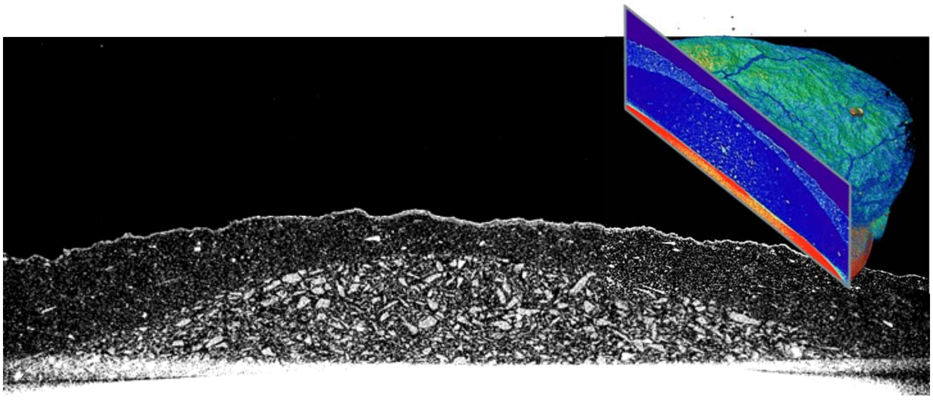
Radiography:



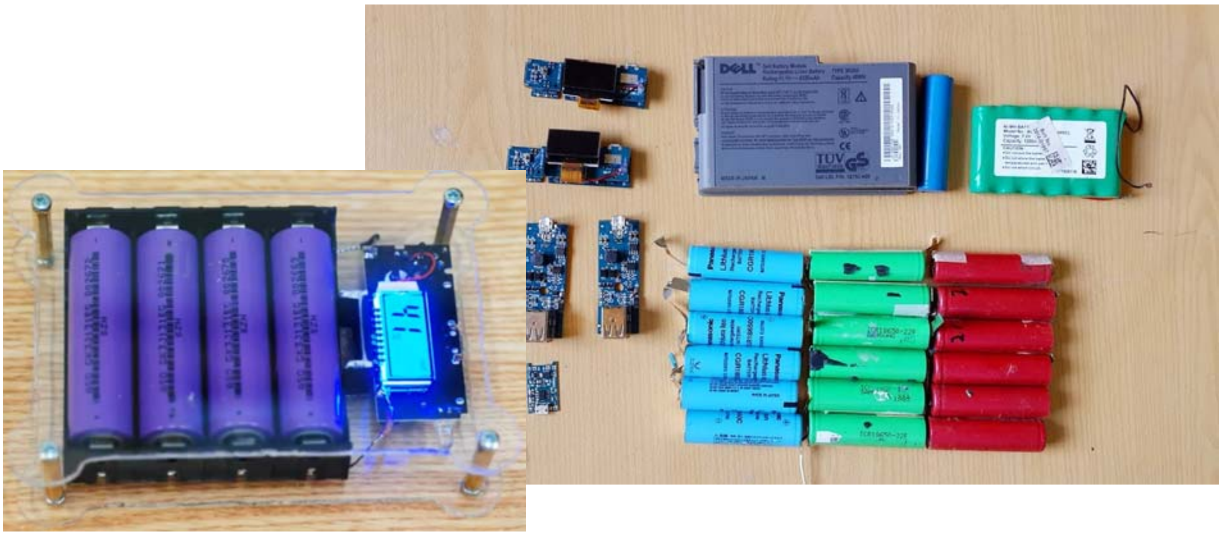
Reconstructed volume:



EX-SITU ANALYSIS OF THE CELL

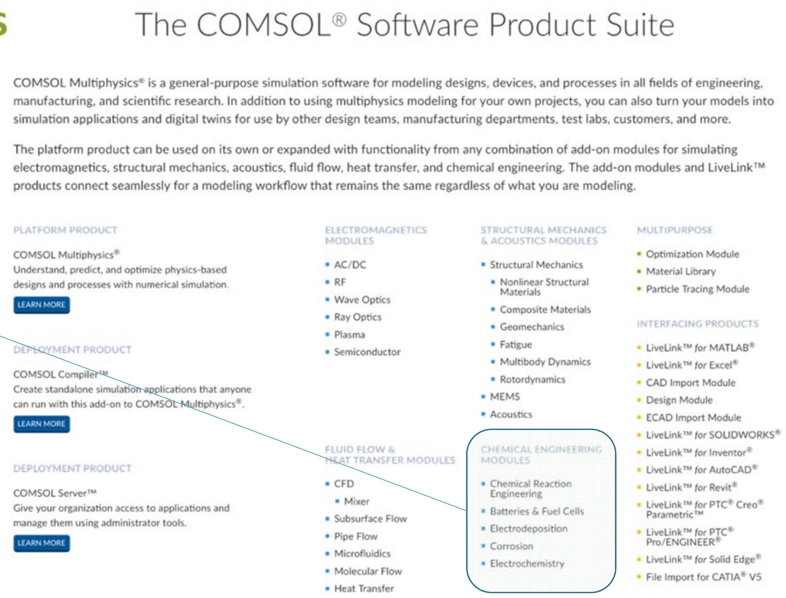


Reusing 18650 LIBs for "home made Power Banks"



Images from this link

Comsol multiphysics



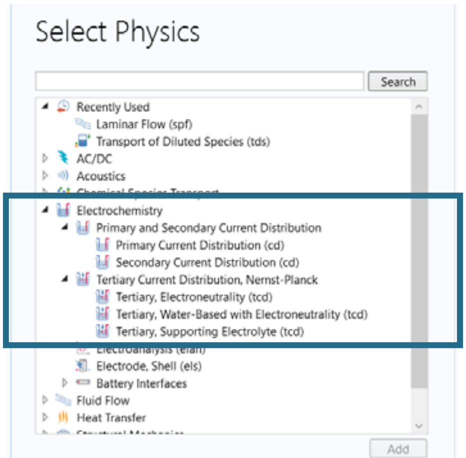
CHEMICAL ENGINEERING MODULES

- Chemical Reaction Engineering
- Batteries & Fuel Cells
- Electrodeposition
- Corrosion
- Electrochemistry

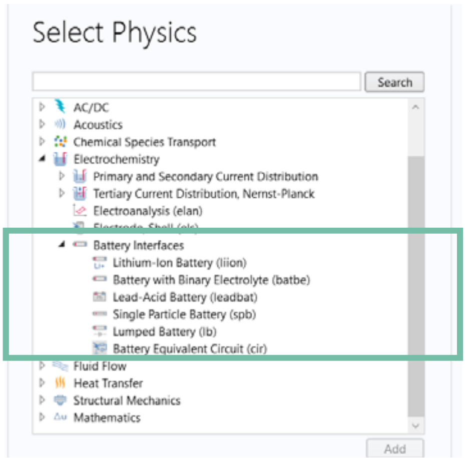
juanma.paz@uma.es

COMSOL Multiphysics modules

Electrochemistry



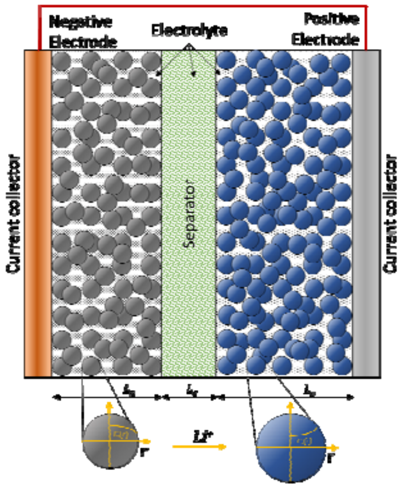
Battery Interface



juanma.paz@uma.es

UNIVERSIDAD DE MÁLAGA

Newman's pseudo-bidimensional Model for LIBs (I)

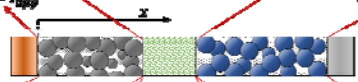


Mass and Charge in the electrolyte

$$\varepsilon_i \frac{\partial c_{2,i}}{\partial t} = \frac{\partial}{\partial x}\left(D_{\text{eff},i}\frac{\partial c_{2,i}}{\partial x}\right) + (1 - t_+^0)a_i J_i$$

$$-\frac{\partial}{\partial x}\left(\kappa_{\text{eff},i}\frac{\partial \phi_2}{\partial x}\right) + \frac{2RT(1-t_+^0)}{F}\frac{\partial}{\partial x}\left(k_{\text{eff},i}\frac{\partial(\ln c_i)}{\partial x}\right) = a_i F J_i$$

Boundary conditions:



$$-\sigma_{eff,p}\frac{\partial \phi_{1,p}}{\partial x^2}\Big|_{x=L_p} = 0$$

$$-\sigma_{eff,n}\frac{\partial \phi_{1,n}}{\partial x^2}\Big|_{x=L_p+L_s} = 0$$

$$-\sigma_{eff,p}\frac{\partial \phi_{1,p}}{\partial x^2}\Big|_{x=0} = I_{app}$$

$$-\sigma_{eff,n}\frac{\partial \phi_{1,n}}{\partial x^2}\Big|_{x=L_p+L_s+L_n} = 0$$

$$-D_{eff,p}\frac{\partial c_{2,p}}{\partial x}\Big|_{x=0} = 0$$

$$-D_{eff,n}\frac{\partial c_{2,n}}{\partial x}\Big|_{x=L_p+L_s+L_n} = 0$$

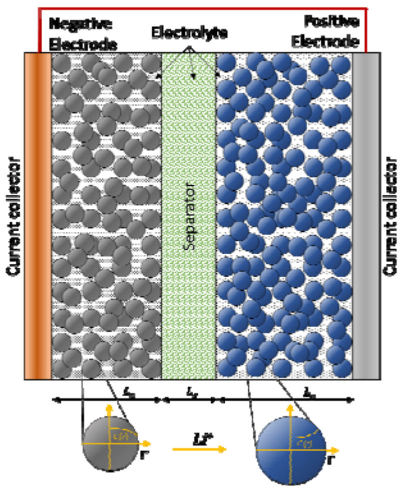
$$c_{2,p}\Big|_{x=L_p^-} = c_{2,s}\Big|_{x=L_p^+}$$

$$c_{2,s}\Big|_{x=(L_p+L_s)^-} = c_{2,n}\Big|_{x=(L_p+L_s)^+}$$

$$-D_{eff,n}\frac{\partial c_{2,p}}{\partial x}\Big|_{x=L_p^-} = -D_{eff,n}\frac{\partial c_{2,s}}{\partial x}\Big|_{x=L_p^+}$$

$$-D_{eff,s}\frac{\partial c_{2,s}}{\partial x}\Big|_{x=(L_p+L_s)^-} = -D_{eff,n}\frac{\partial c_{2,n}}{\partial x}\Big|_{x=(L_p+L_s)^+}$$

Newman's pseudo-bidimensional Model for LIBs (II)

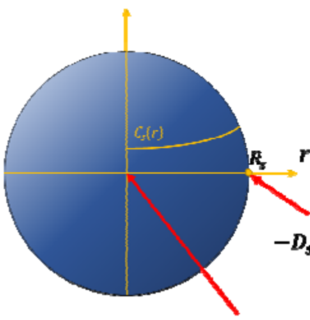


Mass Balance in solide particles

$$\frac{\partial c_{1,i}}{\partial t} = D_{s,i}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c_{1,i}}{\partial r}\right)$$

Charge Balance in the solid phase

$$-\sigma_{\text{eff},i}\frac{\partial \phi_{1,i}}{\partial x^2} = a_i F J_i$$



$$-D_{s,i}\frac{\partial c_{1,i}}{\partial r}\Big|_{r=R_{s,i}} = J_i$$

$$-D_{s,i}\frac{\partial c_{1,i}}{\partial r}\Big|_{r=0} = 0$$

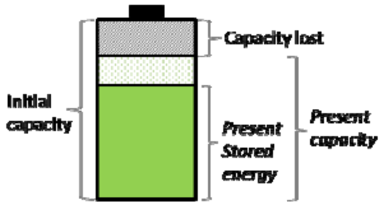
Lithium-Ion Batteries: Results

Battery parameters

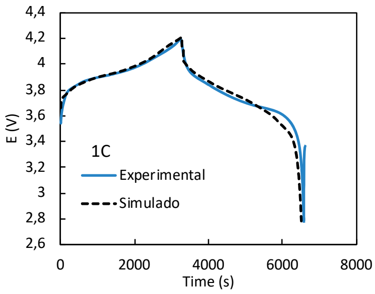
Theoretical stored energy: $\xi = \int_0^t E_{cell}\, dt \cdot I$

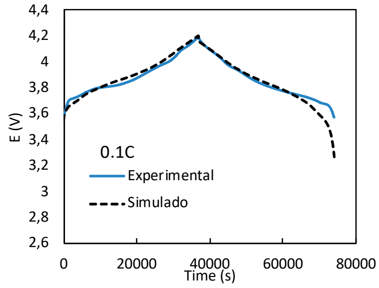
State of Charge : $SoC(t) = \frac{\text{Energy storaged}}{\text{Present capacity}}$

State of Health : $SoH = \frac{\text{Present capacity}}{\text{Initial capacity}}$



LiPo cell and Ivium VertexOne

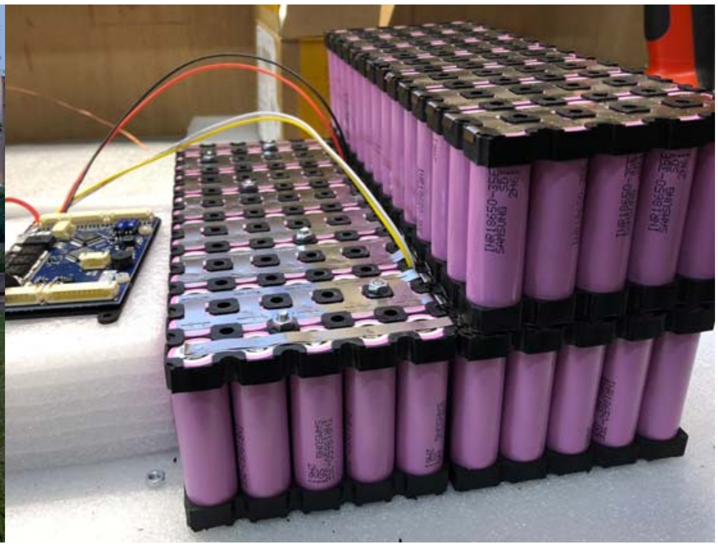




juanma.paz@uma.es

UNIVERSIDAD DE MÁLAGA

Second life of batteries

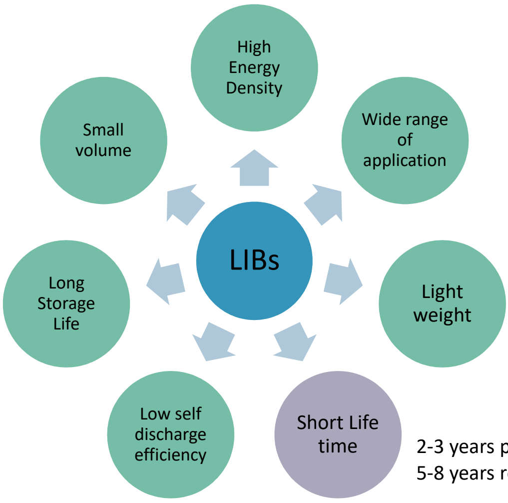


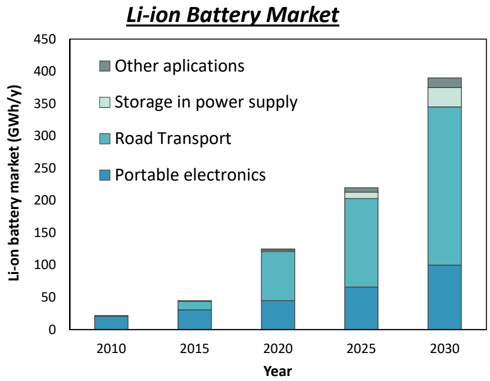
Images from this link

juanma.paz@uma.es

UNIVERSIDAD DE MÁLAGA

Introduction: Lithium-Ion Batteries (LIBs)





2-3 years portable electronics
5-8 years road transport

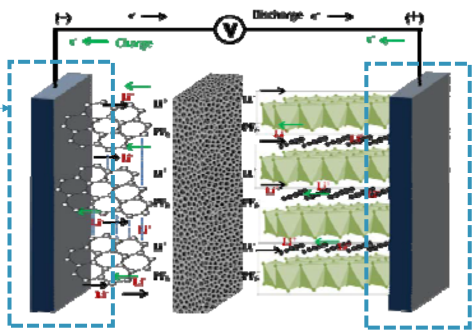
Waste LIBs

juanma.paz@uma.es

LIBs components

Anode:
- Graphite
- $Li_4Ti_5O_{12}$

Electrolyte:
$LiClO_4$, $LiPF_6$, $LiBF_4$, PC and DEC



Cathode:
- LCO: $LiCoO_2$
- LMO: $LiMn_2O_4$
- NCM: $LiNi_xCo_yMn_{1-x-y}O_2$
- NCA: $LiNiCoAlO_2$
- LFP: $LiFePO_4$

Separator
Polypropilene

Highly Valuable Components → Cobalt, Phosphate and Graphite is considered as a **Critical Raw Material** → **Recycling Batteries to recovery metals**

juanma.paz@uma.es

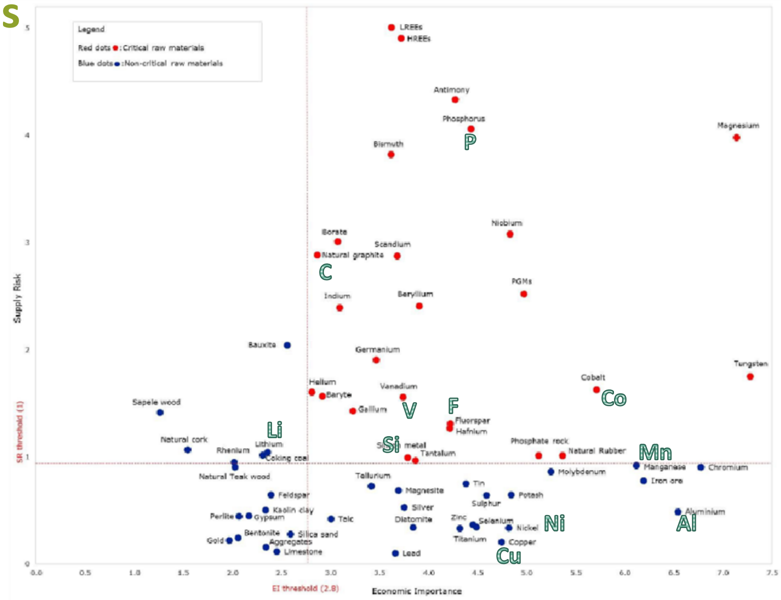
Critical Raw Materials

The 2017 criticality assessment was carried out for 61 candidate materials (58 individual materials and 3 material groups: heavy rare earth elements, light rare earth elements, platinum group metals, amounting to 78 materials in total.

- **Economic importance -** aims at providing insight into the importance of a material for the EU economy in terms of end-use applications and the value added (VA) of corresponding EU manufacturing sectors at the NACE rev.2 (2-digit level).

- **Supply risk -** reflects the risk of a disruption in the EU supply of the material. It is based on the concentration of primary supply from raw materials producing countries, considering their governance performance and trade aspects. Depending on the EU import reliance (IR), proportionally the 2 sets of the producing countries are taken into account — the global suppliers and the countries from which the EU is sourcing the raw materials.

Figure A: Economic importance and supply risk results of 2017 criticality assessment



https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_es

juanma.paz@uma.es

LIBs recycling

LIBs recycling is focused on:

✓ Reduce the environmental impact caused by waste LIBs

✓ Recovery LIBs components to reuse them

PYROMETALLURGICAL		HYDROMETALLURGICAL	
High temperature smelting reduction		Acidic leaching + separation	
Advantages	**Disadvantages**	**Advantages**	**Disadvantages**
- Great Capacity - Simple operation	- High temperature - High Energy consumption - Low metal recovery rate	- Low energy consumption - High metal recovery - High product purity	- Long recovery process - High chemical reagents consumption

Development of more efficiencies recycling technologies

juanma.paz@uma.es

Some recent facts about LIB recycling

- More than 75% of research on LIB recycling has been done on hydrometallurgical processes
- 70 % were carried out by scientists from China of Sourth Korea
- Most research studies have been cofused on LCO and NCM, and just a few on LFP, LMO and NCA. Barely other research on new generatino of batteries, such as Na-IB, or Al-IB
- Results indicate that active materials inlcuding Li and Co can be recycled with high efficiency

Electrokinetic remediation for e-waste

Electrokinetic Remediation **(EKR)**

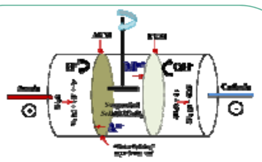
↓

Electrodialytic Remediation **(EDR)** → **Applications:**

Polluted soils
Wastewater sludge
Mine tailing
Harbor sediments
…

Proposal:
New application → **Recycling of Electronic Waste**

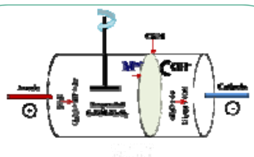
Electrodialytic experiments: Trial and Error



- 3 compartment ED cell
- Membranes: 1 AEM + 1 CEM
- $LiCoO_2$ powder suspended in the central compartment
- Current: 500 mA
  (Full extraction in 4 hours)

3C ED Cell

↓ **Current AEM**



- 2 compartment ED cell
- Membranes: 1 CEM
- $LiCoO_2$ powder suspended in the anode compartment
- Current: 50 mA
  (Full extraction in 40 hours)

2C ED Cell

External stirring

EXTERNAL EXTRACTION + ELECTRODIALYSIS

RESULTS 3C ED Cell:
- **Power source saturation in 1 hour**
- $LiCoO_2$ was not dissolved
- Current was transported only by H^+ and Cl^-

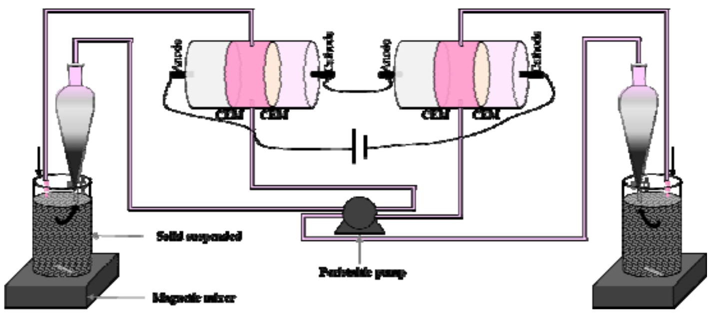
RESULTS 2C ED Cell:
- Extraction below 2%
- $LiCoO_2$ solid particles got fixed to the cell walls and membrane.

juanma.paz@uma.es

Electrodialytic experiments

EXTERNAL EXTRACTION + ELECTRODIALYSIS

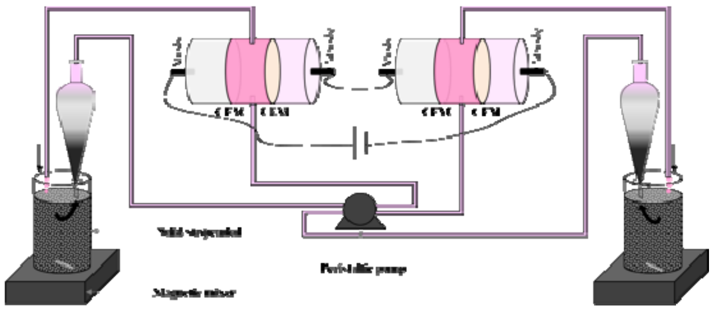
- **3 compartment ED cell**
- Membranes: **2 CEM**
- Current: **50 mA (4-5 days)**



Process:

1) $LiCoO_2$ stirred in a external vessel
2) Decantation funnel was used as upward-flow sedimenter. Suspended solid solution passed through it.
3) Stream leaves was connected to the central compartment cell.
4) Two cell connected in series were used to ensure the electric current was the same in both cell

juanma.paz@uma.es



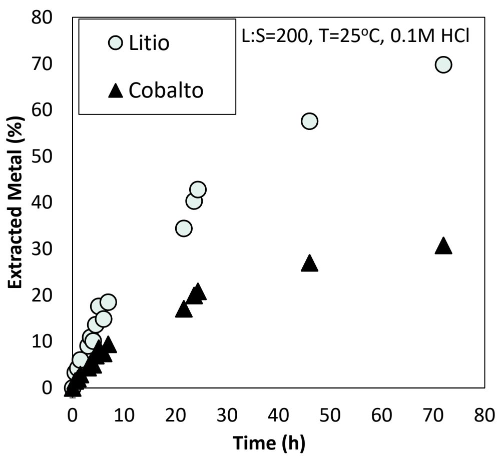
Extraction analysis

- **Extractant agent**: 0.1M HCl
- **Solid:** $LiCoO_2$ commercial
- **L/S:** 200
- **Temperature:** 25ºC
- Batch stirring

$$\%\text{Metal extraction} = \frac{\text{Metallic ion dissolved}}{\text{Total amount of Metal in } LiCoO_2} \cdot 100\%$$

Conclusion:

- Kinetics of the particle solution is moderately slow.
- Non-equimolar proportion of Li and Co extracted.



juanma.paz@uma.es

Non-equimolar proportion of Li and Co extracted

✓ **Dissolution of particles**

$$2LiCoO_2 + 8HCl \rightleftarrows 2LiCl + 2CoCl_2 + 4H_2O + Cl_2$$

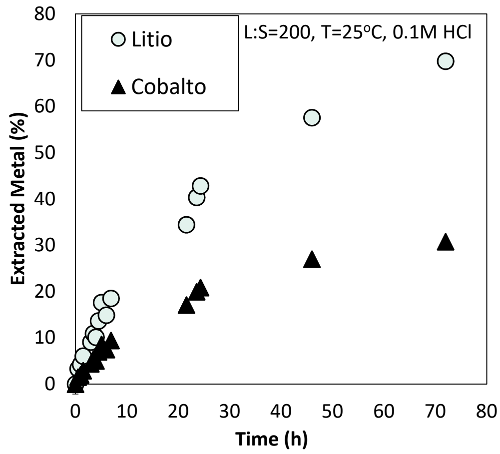
✓ **Ion exchange and Co(II,III) oxide formation**

$$LiCoO_2 + HCl \rightleftarrows HCoO_2 + LiCl$$

$$3HCoO_2 \rightleftarrows Co_3O_4 + H_2O$$

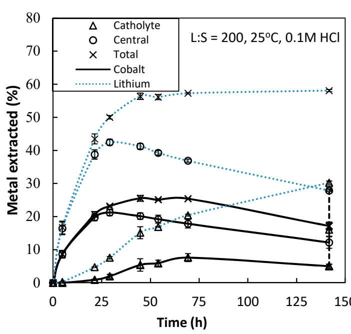
✓ **Future work: use of reducing agents**

$$Co^{3+} + H_2O_2 \rightleftarrows Co^{2+} + H_2O + \frac{1}{2}O_2$$

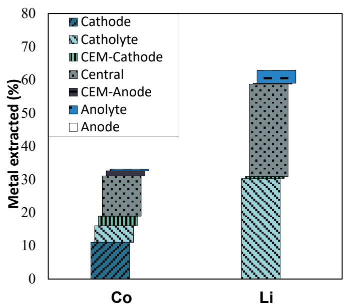


Electrodialytic experiments

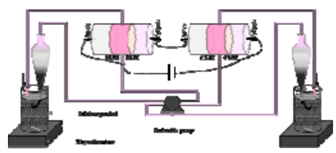
RESULTS: External extraction + Electrodialysis



Time-transient values for %extracted metal in the central and catholyte compartment.



%Co and %Li in the different parts of the ED cell at the end of the experiment



Selective recovery of Cobalt and Lithium:

- Cobalt electrodeposited in cathode surface.
- Lithium accumulated in the catholyte compartment.

Future works

- Extraction analysis using different extractant agents (HNO_3, Acetic Acid, Nitric Acid…).
- Use of reductant agent to enhance the metal extraction.
- Characterization of real lithium-ion batteries.

- Electrodialytic metal recovery from batteries with different cathode electrode.

juanma.paz@uma.es

UNIVERSIDAD DE MÁLAGA

Reusing and Recycling of Secondary Batteries

M.M. Cerrillo-Gonzalez, M. Villen-Guzman, **J.M. Paz-Garcia**

Department of Chemical Engineering
University of Malaga (Spain)

THANK YOU!

UNIVERSIDAD DE MÁLAGA