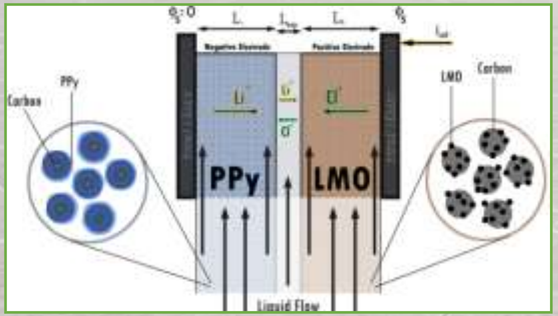
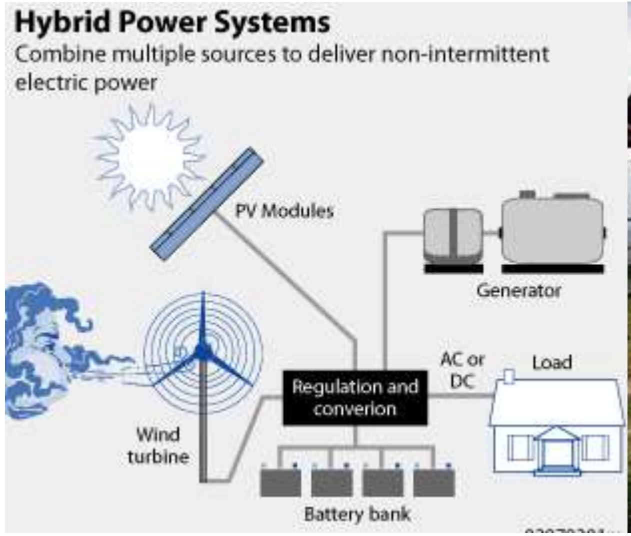
Nanotechnology for energy storage and for Sustainable extraction of lithium from natural brine

Ernesto Julio Calvo
INQUIMAE. UBA-CONICET

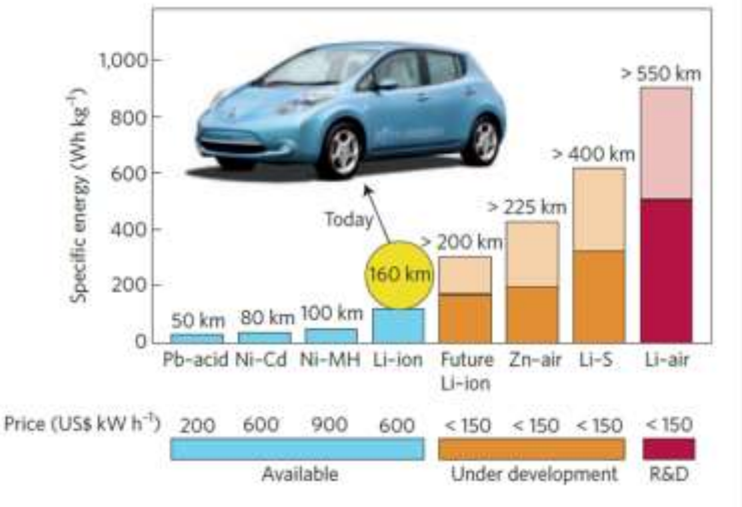




Remote Electrification (7.5 GWh market in South America)

Portable Electronics

Why is Lithium strategic for Energy Storage?



Electric Vehicles

Li-ion battery market 2016 87 GWh

PORTABLE ELECTRONICS (1990´s-2010´s)

Mobile Phones
Smart Phones (iphone)
Tablets

Increasing battery capacity (saturated market)

ELECTRIC VEHICLES (Emission Targets)

Hybrid
Plug.-in
Full electric (XEVs) (Tesla)- Electric Bus China

2012	7%	Li-ion batteries
2014	27%	“
2016	50%	“
2026	1 TWh (1000 GWh)	

Source: Roskill Report

25,000 cars in the quarter january-march. 2017 500.000 in 2018

Lithium Batteries for Electric Car

450 kg battery 400 V cc. 60/75/90 kW (156 Wh/kg)
7104 cellx x 2,4 V = 17.050 Ah
4,453 g Li

Lithium Battery for a cell phone

4.9 Wh
1.32 mAh
0.344 g

With the mass of lithium in 1 car we can store the energy of 17.000 cell phones

GIGAFACTORY TESLA

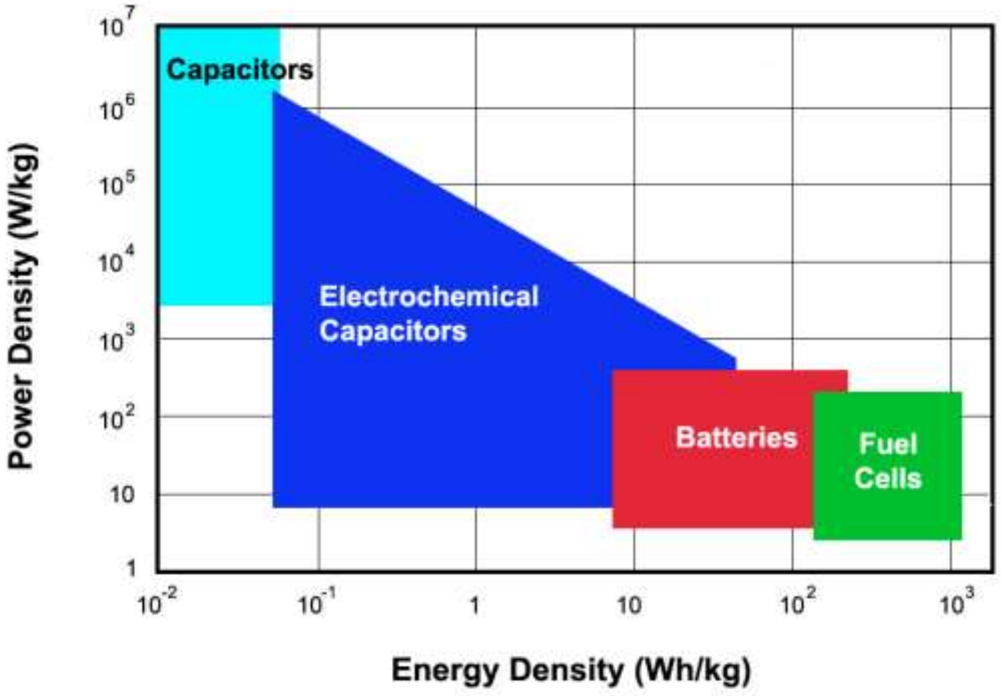
Electric Avenue. Sparks, NV 89434, EEUU

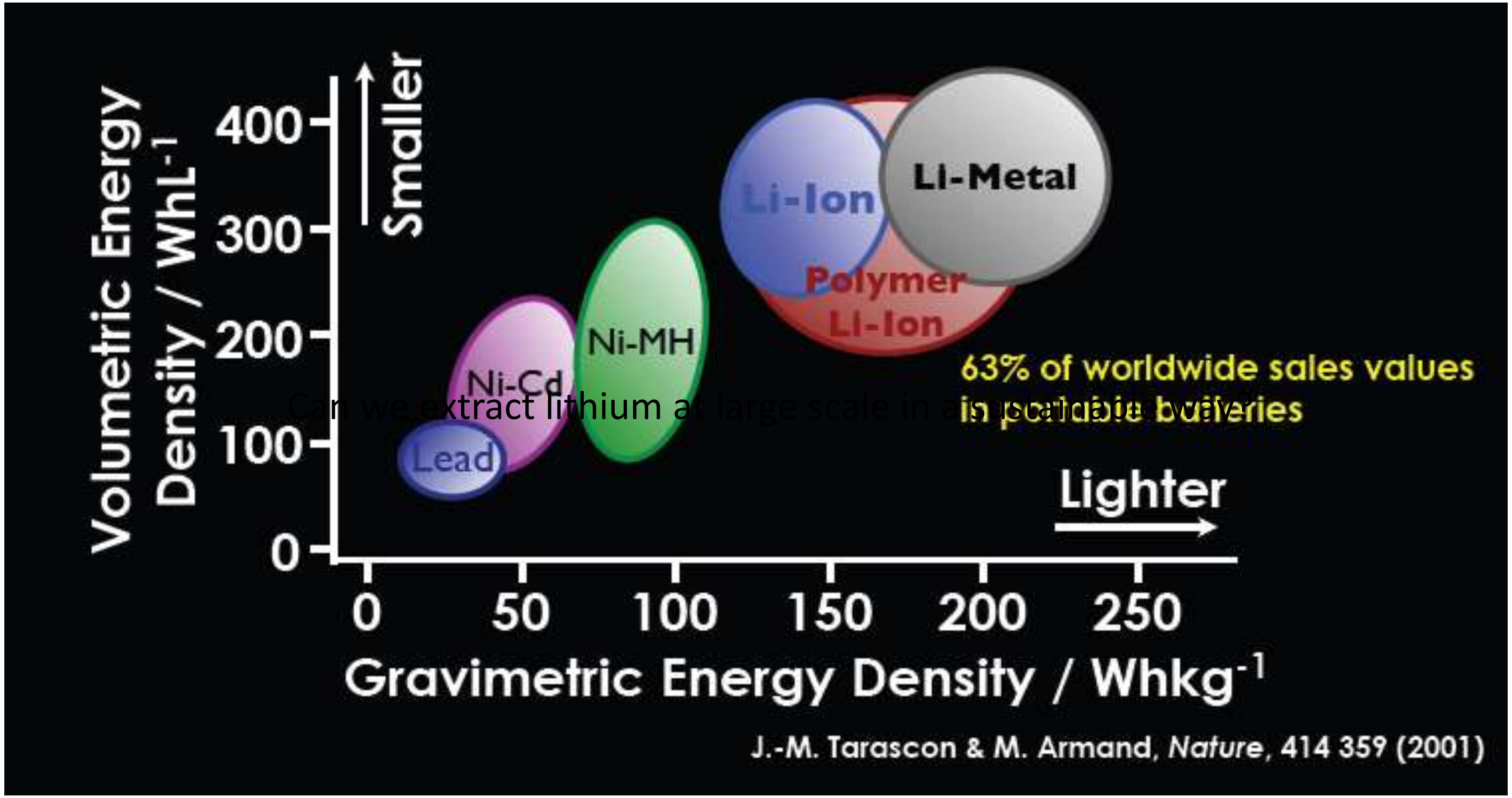
Tesla plans to manufacture 500.000 electric cars in 2018 (aprox. 2.250 ton of litium)

BATERÍAS

- Las baterías almacenan energía en compuestos químicos capaces de generar carga eléctrica.
- Poseen alta densidad de energía.
- Existe una gran variedad de baterías.

- Baterias Primarias (No recargables)
- Zn/carbon 1,5 V, 0,13
- Zinc/aire 1,4 V
- Zn/MnO_2 (alcalinas), 1, 5 V
- Li/O_2, 2,91 V
- $Li\text{-}SOCl_2$, 3,5 V
- Baterias Secundarias (Recargables)
- PbO2/PbSO4, 2,1 V
- Ni/Cd, 1,2 V
- Ni/MHx (AA), 1,2 V, 1,3 Ah
- $C_6Li_x/LiCoO_2$, 3,7 V
- Li/LiFePO4, 3,3 V
- Li/O_2, 2,91 V (futuro para vehículos)





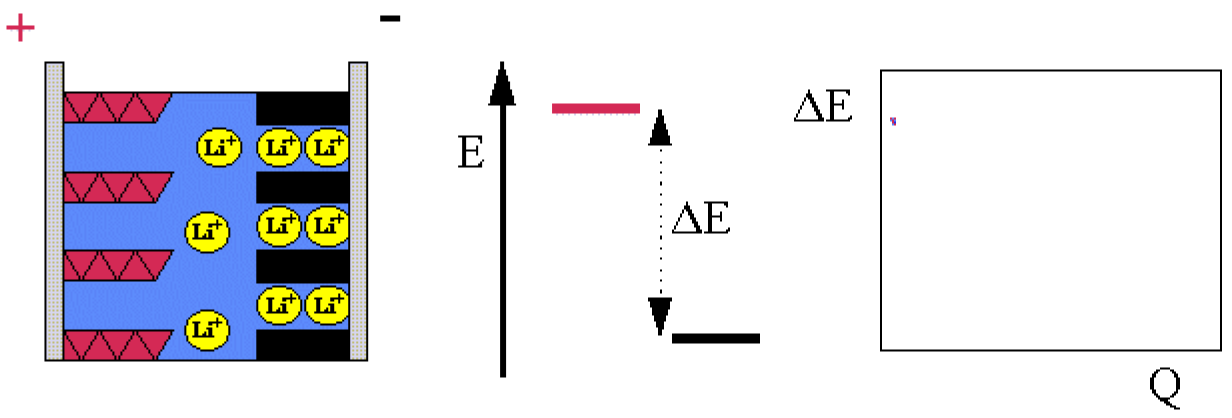
Can we extract lithium at large scale in a sustainable way?

Baterías de ion litio (sony 1991)

All reactions occur at the interface
Whatever this is : flat or pores…..

$LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$

Cathode

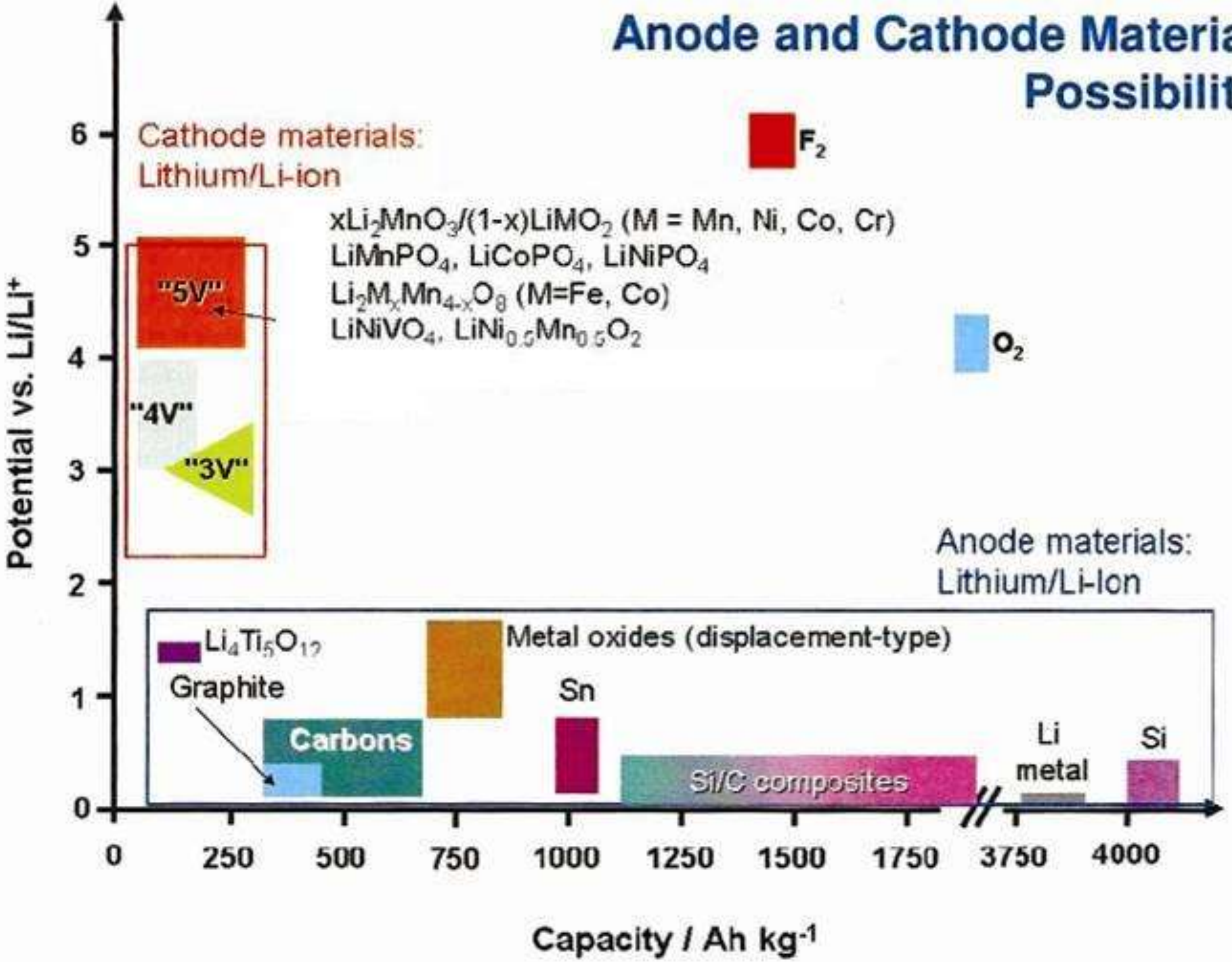


$C + xLi^+ + xe^- \leftrightarrow Li_xC$

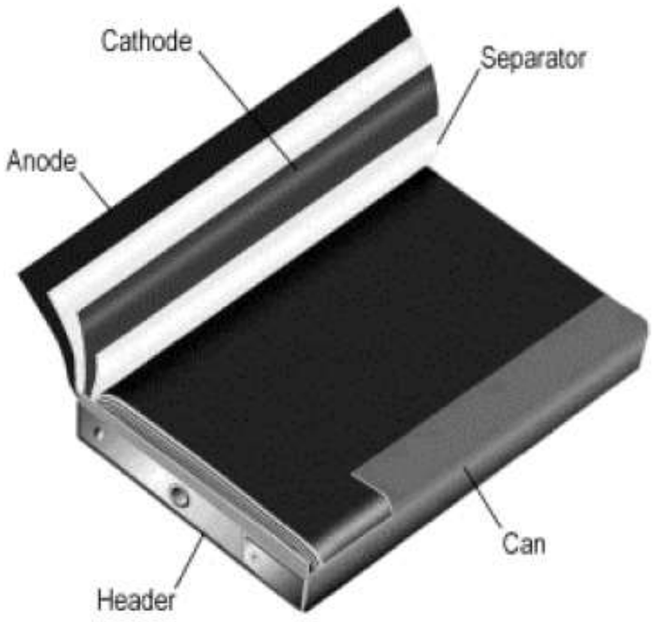
Anode

Ion diffusion : Interfaces
→ Particle size and NANO

Anode and Cathode Materials: Possibilities

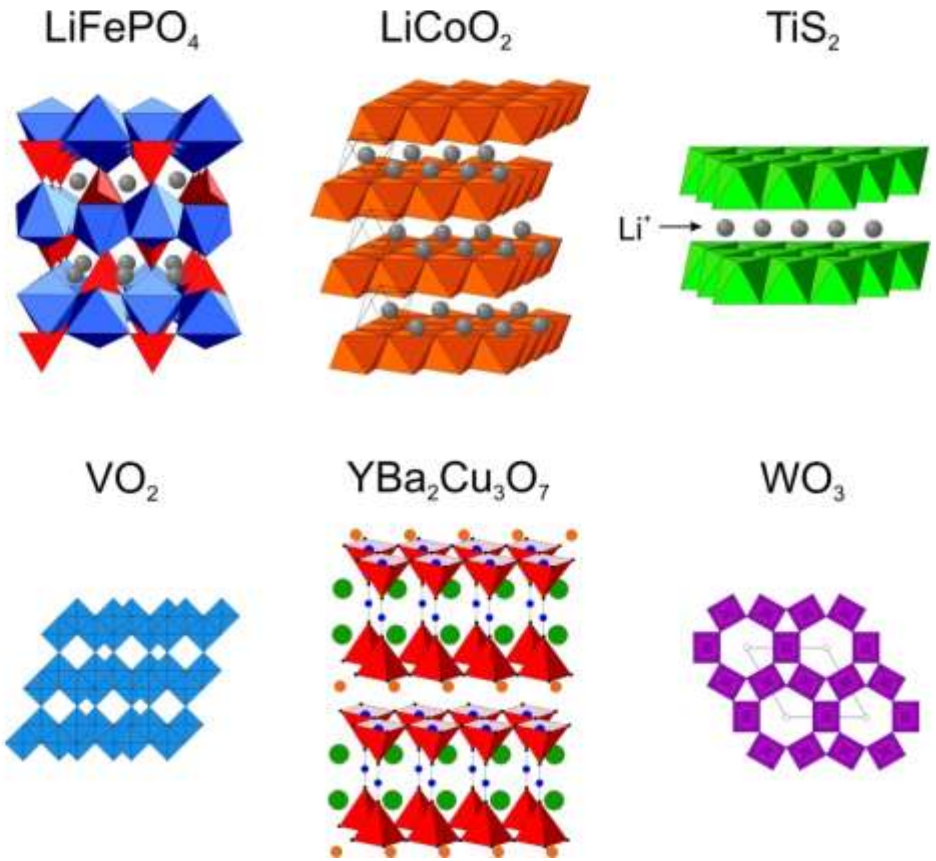


Cathode Materials



igure 3-3: Cross-section of a prismatic cell.

Intercalation compounds
John Goodenough, 1980´s



Journal of The Electrochemical Society, 160 (1) A15-A24 (2013)
0013-4651/2013/160(1)/A15/10/$28.00 © The Electrochemical Society

Effects of Nanoparticle Geometry and Size Distribution on Diffusion Impedance of Battery Electrodes

Juhyun Song[a] and Martin Z. Bazant[a,b,*,z]

[a]Department of Chemical Engineering and [b]Department of Mathematics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

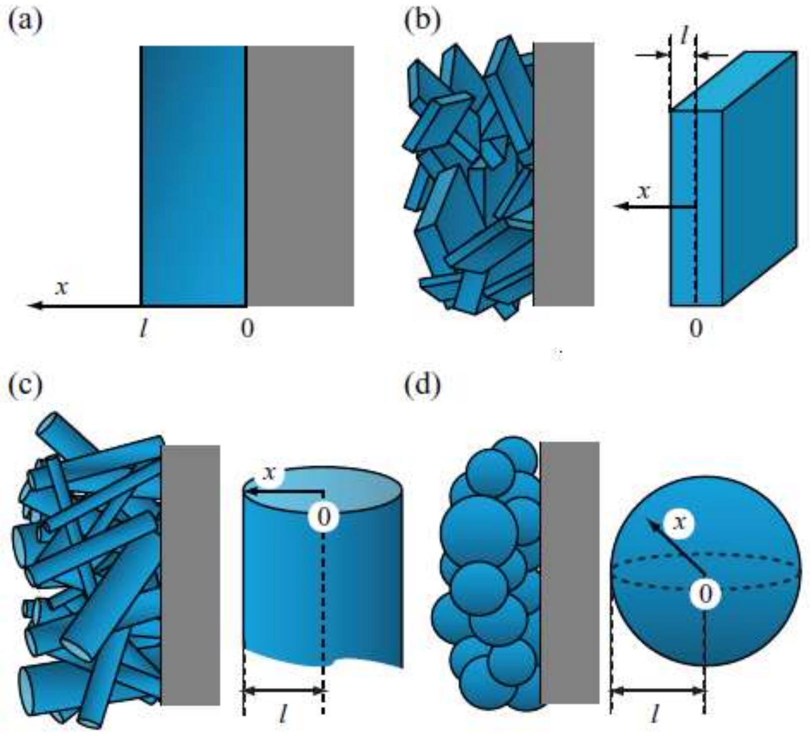


Figure 1. Model electrode configurations, particle geometries, and corresponding coordinate systems, where the blue region and the gray region represent the active material and the current collector, respectively: (a) thin film electrode, (b) electrode with planar particles, (c) electrode with cylindrical particles, and (d) electrode with sphere particles.

$$\frac{\partial c}{\partial t} = D_{ch} \nabla^2 c \qquad \hat{j}_{intc} = -eD_{ch} \left. \frac{d\hat{c}}{dx} \right|_{x=l}$$

$LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$
$D_{Li^+} = 10^{-8} - 10^{-10}$ $cm^2.s^{-1}$

$$\frac{l^2}{D_{Li^+}} = \tau$$

Distancia difusional característica:

Con D = 10^{-10} $cm^2.s^{-1}$

Para l = 10^{-4} cm (1 μm) τ = 100 seg

Para l = 10^{-5} cm (100 nm) τ = 1 seg

Para = 10^{-6} cm (10 nm) τ = 0,01 seg

RSC Advances

RSCPublishing

REVIEW

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Recent advances in $LiFePO_4$ nanoparticles with different morphology for high-performance lithium-ion batteries

Cite this: *RSC Adv.*, 2013, **3**, 19744

PHASE TRANSFORMATION

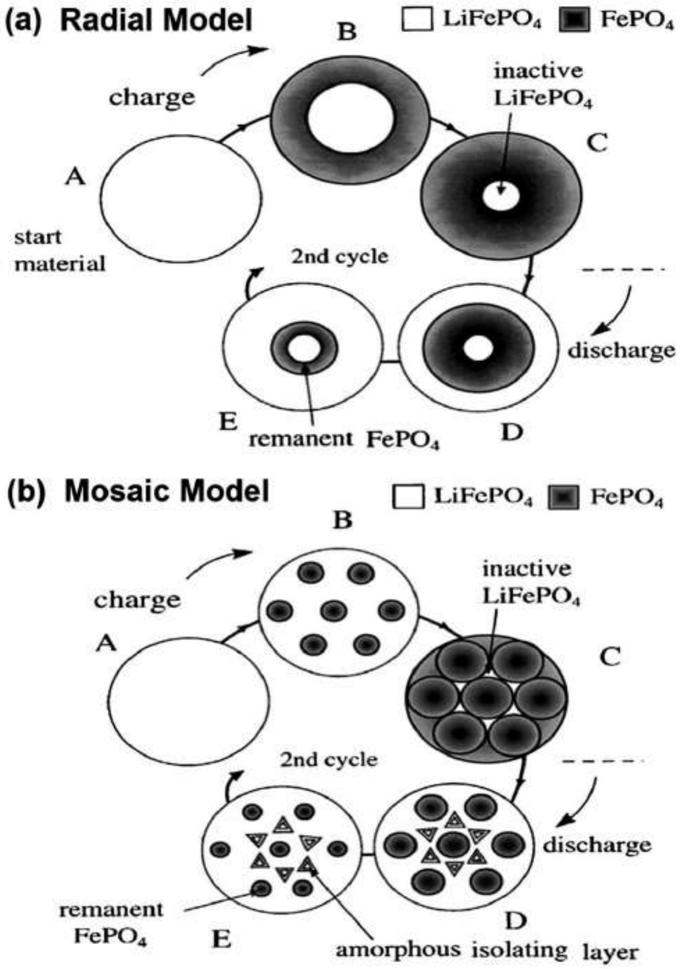
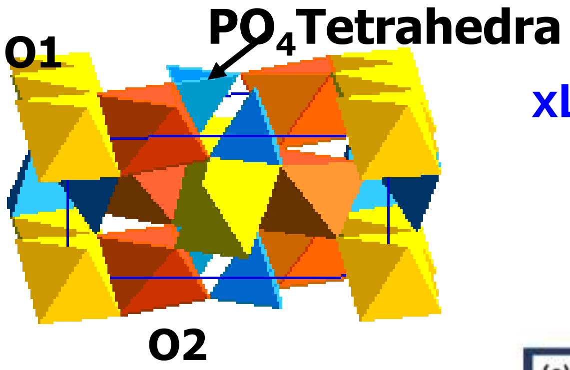


Fig. 3 Schematic models for lithium extraction/reinsertion into a single particle of a $LiFePO_4$ radial model (a) and Mosaic model (b).[56]



10 nm C Nanocoating

$xLi^+ + x\ e^- + MPO_4 \leftrightarrow LiMPO_4$ (M= Fe, Mn, Co, Ni)

- $LiFePO_4$: 3.5V
- $LiMnPO_4$ and $LiMn_{0.8}Fe_{0.2}PO_4$: 4.1V
- $LiCoPO_4$: 4.8V

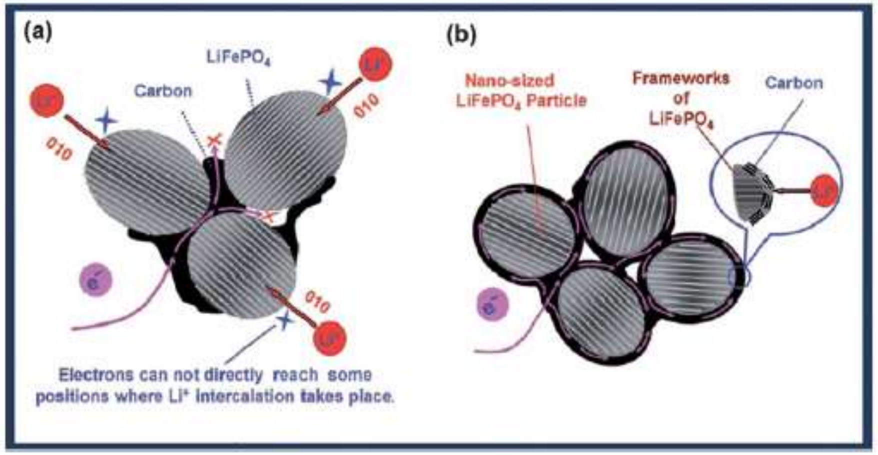


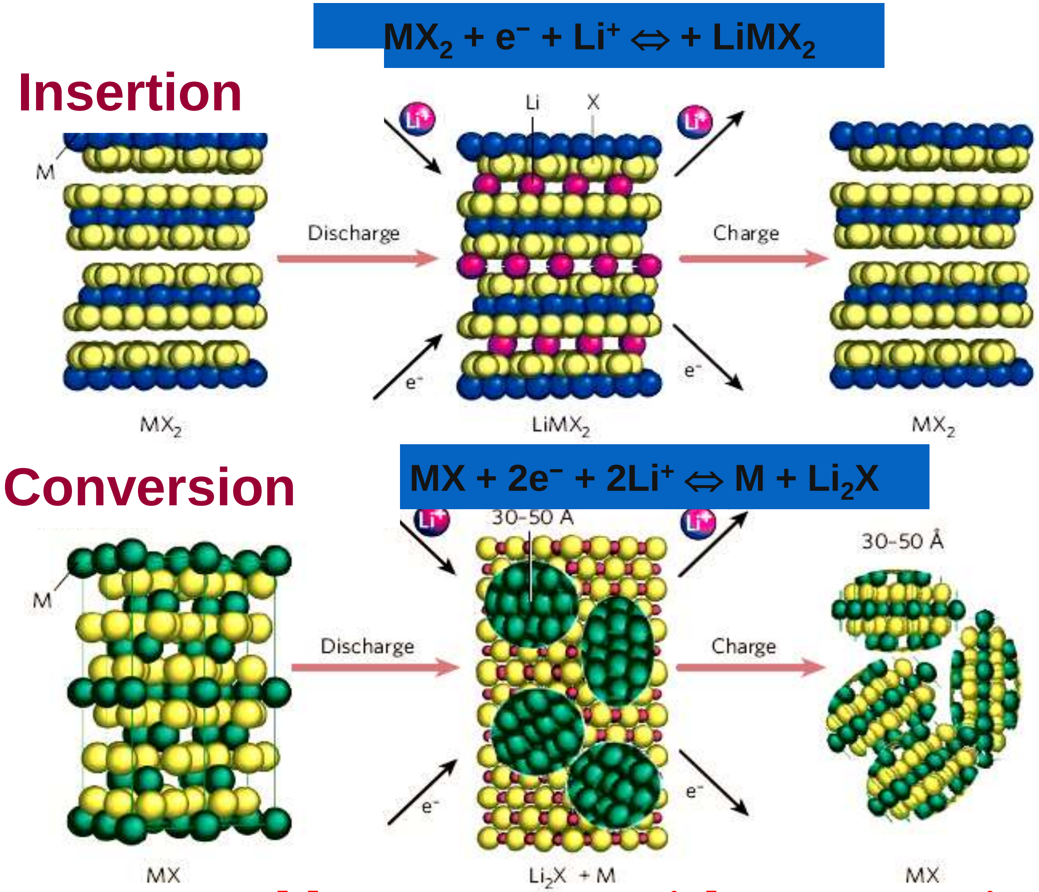
Fig. 4 (a) Electron-transfer pathway for $LiFePO_4$ particles partially coated with carbon. (b) Designed ideal structure for $LiFePO_4$ particles with typical nano-size and a complete carbon coating.[58]

Anodos para baterias recargables de ion litio

$Sn + xe^- + xLi^+ <=> Li_xSn$; x → 4.4 >900mAh/g

$Si + xe^- + xLi^+ <=> Li_xSi$; x → 4.4 > 4000mAh/g

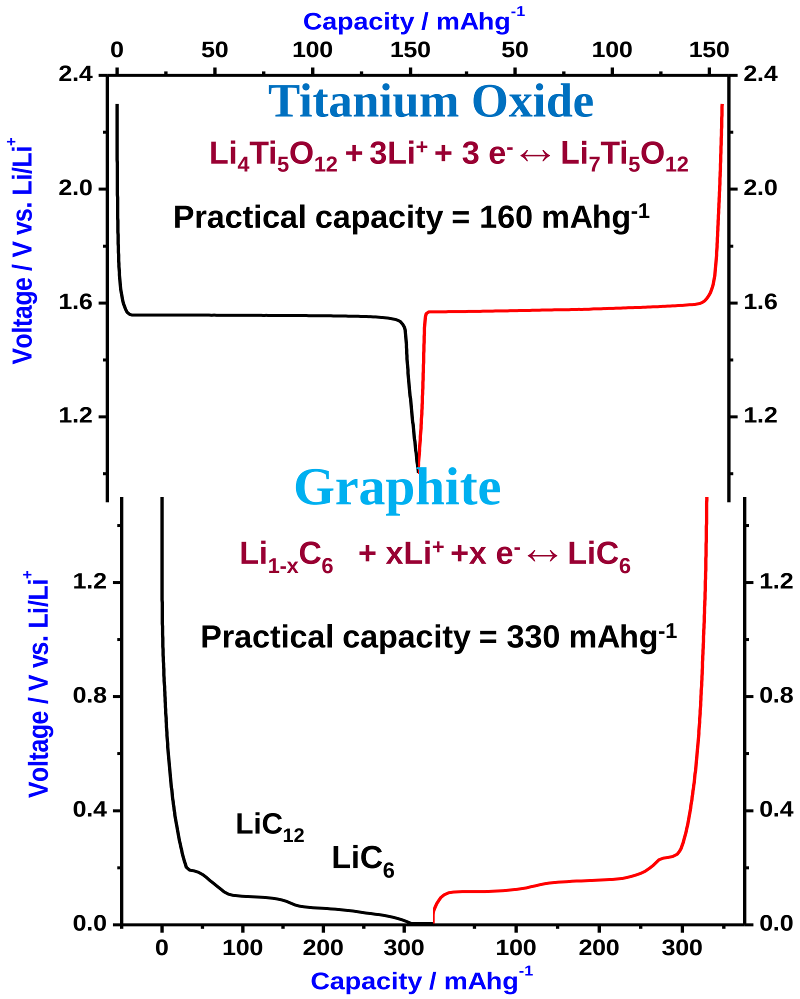
Problem! Nano structures are required



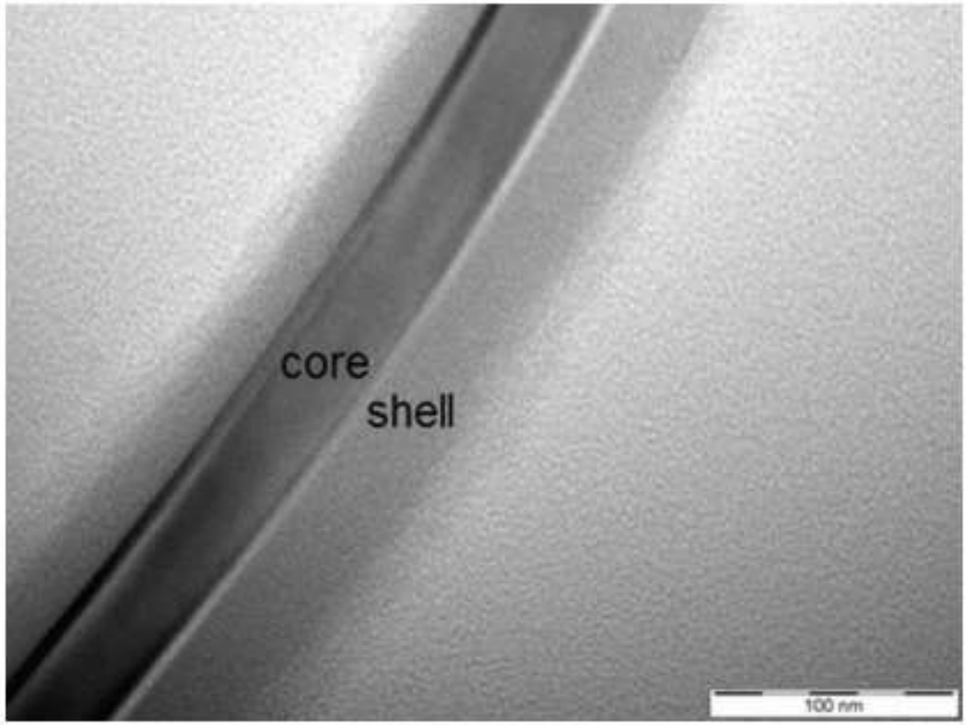
Problem! Nano particles are required

En la actualidad

intercalation compounds



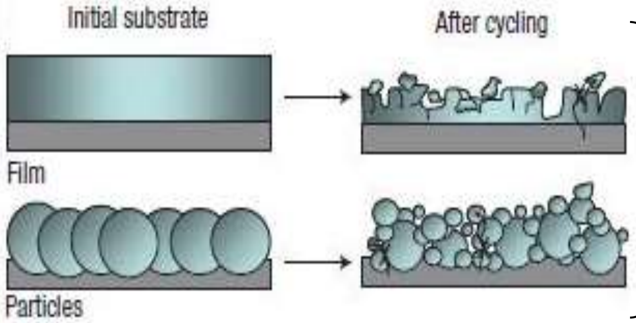
NANO WIRES



- State-of-the-art cells use graphite anodes: (372 mAh/g)
- Germanium, silicon have much higher theoretical capacity (1600, 4200 mAh/g)
- But… 300-400% volume expansion from intercalation – nanowires!

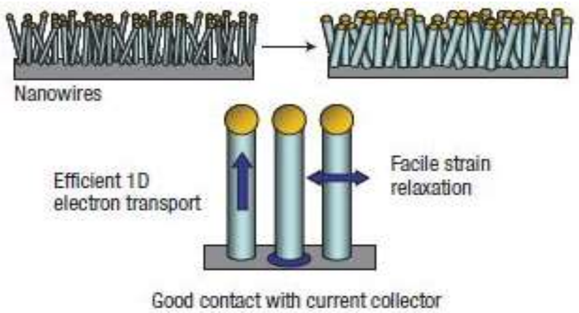
Si-nanostructures for Li-ion batteries

Si-thin films and spherical particles



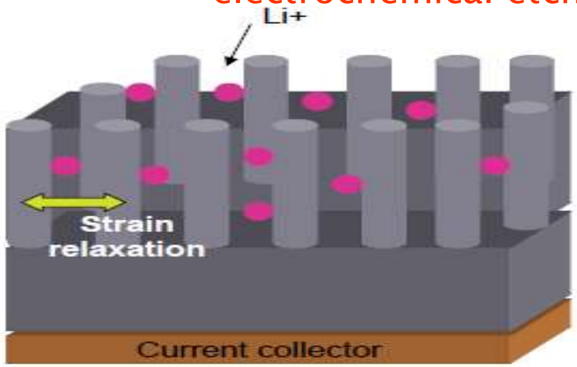
Poor performance

Si-nanowires prepared by CVD



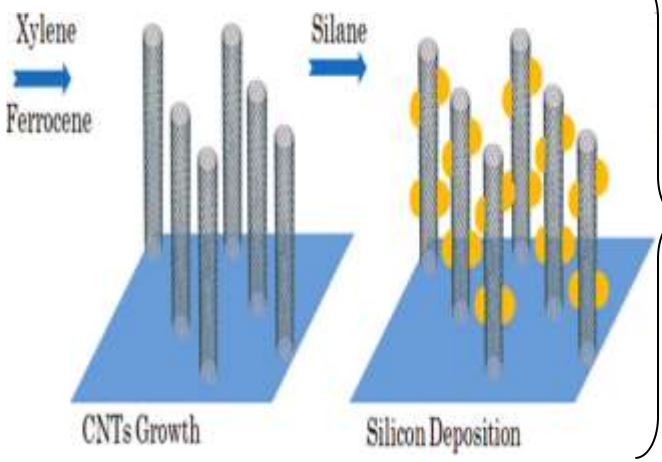
Good performance

Nanoporous-Si prepared through electrochemical etching



Good performance

Si-coated CNT



Good performance

Advantages of SiNWs

1. Small NW diameter accommodate large volume changes.
2. All NW contribute to the capacity.
3. Direct 1D electronic pathways for efficient charge transport.
4. No need for binders (extra weight eliminated).

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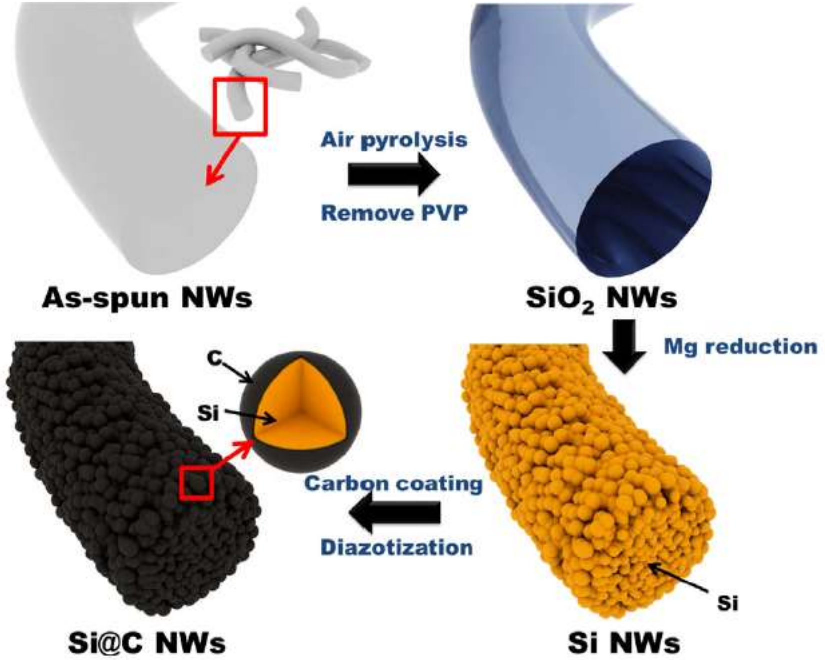
Porous silicon nanowires for lithium rechargeable batteries

Jung-Keun Yoo[1], Jongsoon Kim[2], Hojun Lee[1], Jaesuk Choi[1], Min-Jae Choi[1], Dong Min Sim[2], Yeon Sik Jung[1,3] and Kisuk Kang[2,3]



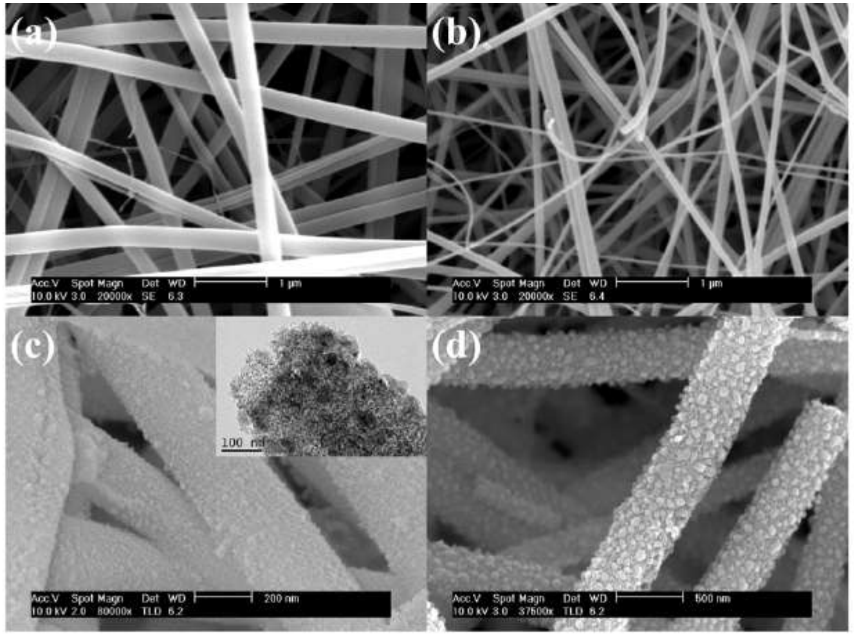


Figure 2. SEM images of (a) as-spun TEOS/PVP nanowires, (b) SiO_2 nanowires after pyrolysis in air, (c) Si nanowires after the Mg reduction and washing steps, and (d) carbon-coated Si nanowires.

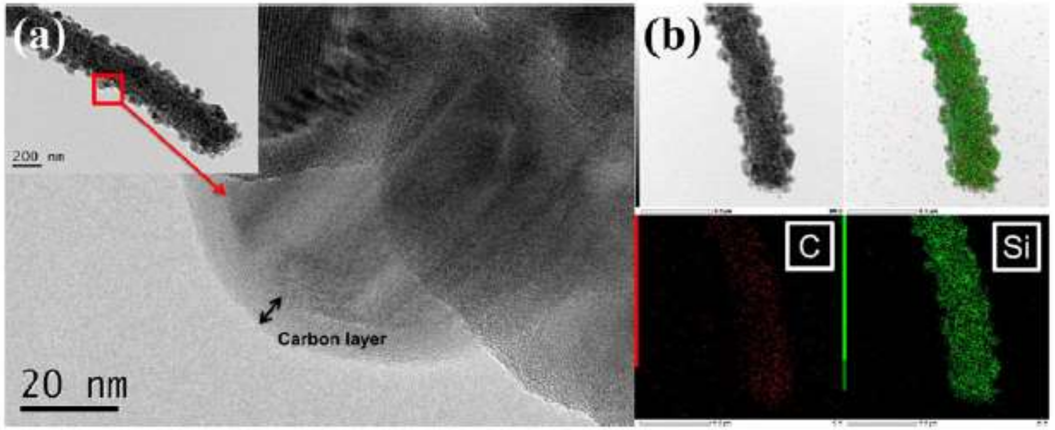
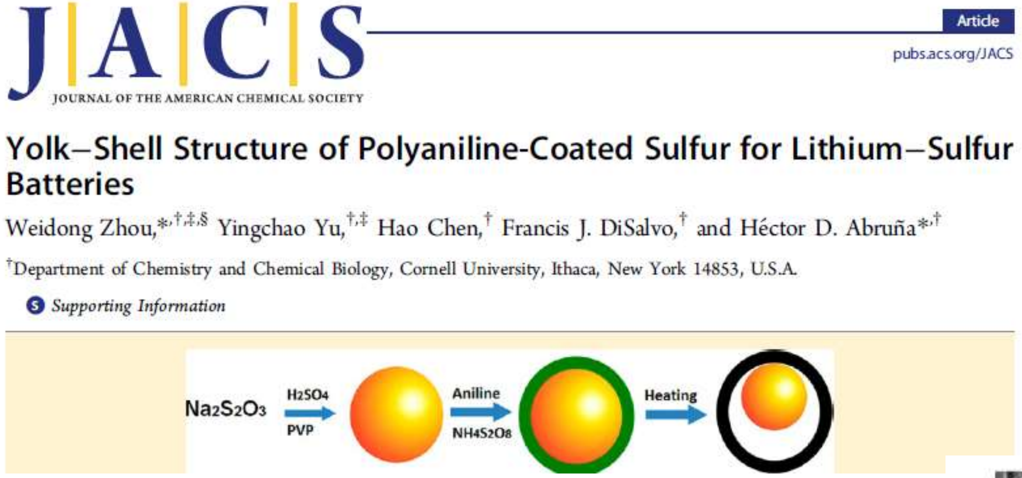


Figure 3. (a) TEM images of carbon-coated Si nanowires. (b) Lower-magnification TEM image and corresponding EDS mapping images of C (red) and Si (green).


J|A|C|S JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
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Yolk–Shell Structure of Polyaniline-Coated Sulfur for Lithium–Sulfur Batteries

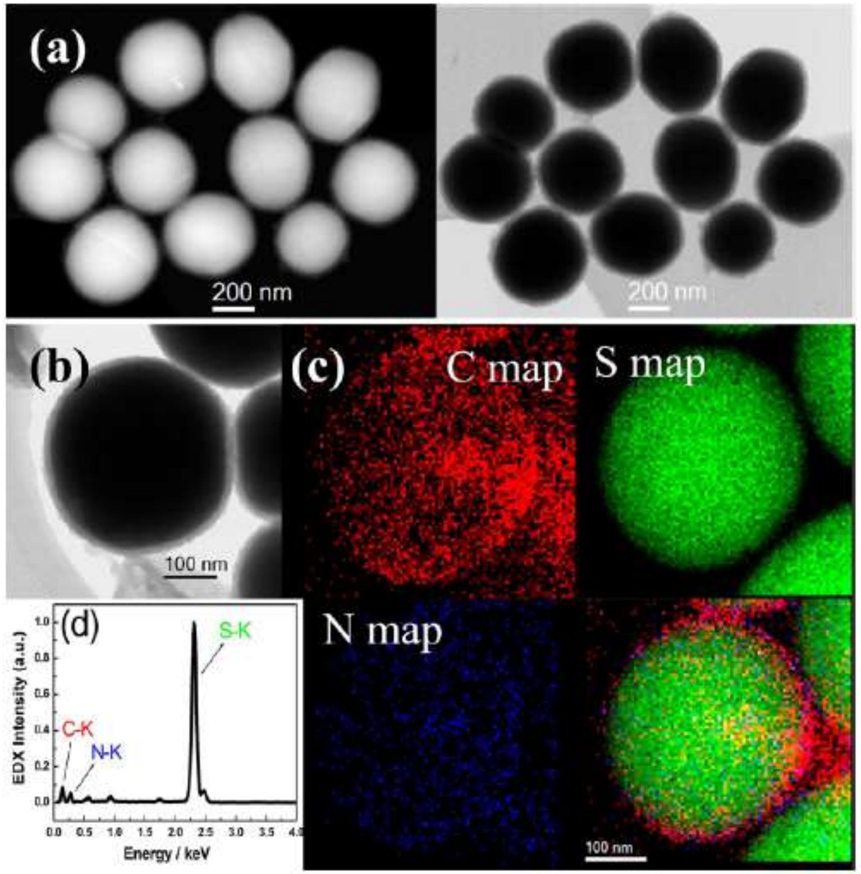
Weidong Zhou,*[†,‡,§] Yingchao Yu,[†,‡] Hao Chen,[†] Francis J. DiSalvo,[†] and Héctor D. Abruña*[†]
[†]Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, U.S.A.
Supporting Information

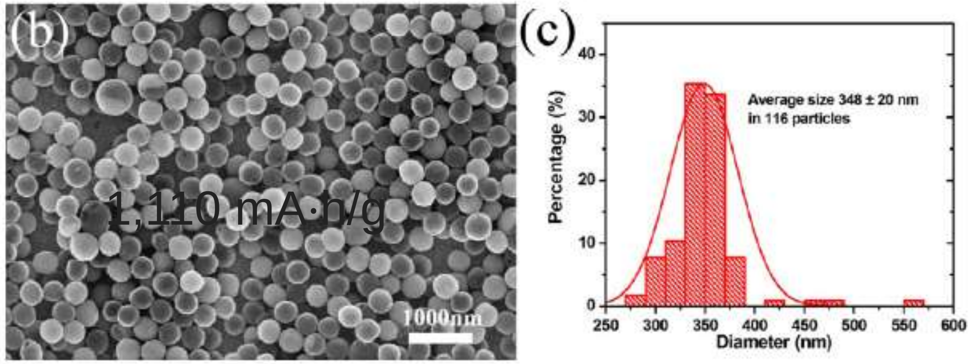
Cathode

$S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_3$

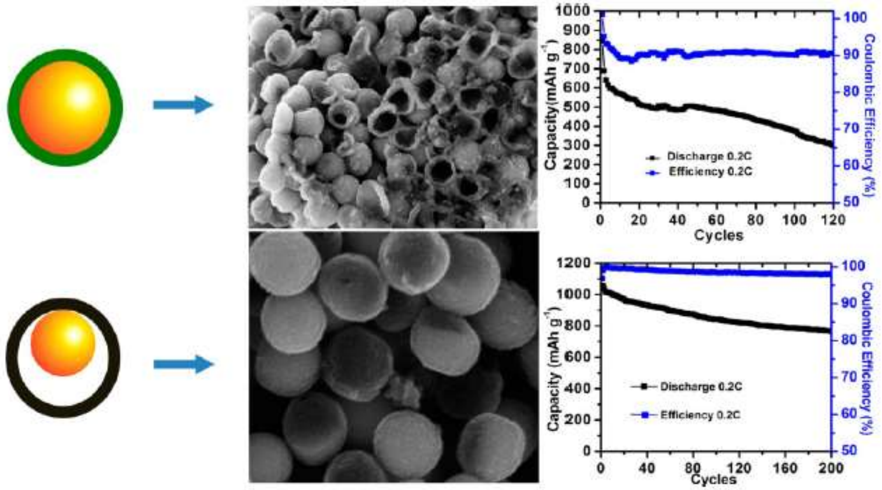
Anode

$Li_2S \rightarrow Li_2S_2 \rightarrow Li_2S_3 \rightarrow Li_2S_4 \rightarrow Li_2S_6 \rightarrow Li_2S_8 \rightarrow S_8$

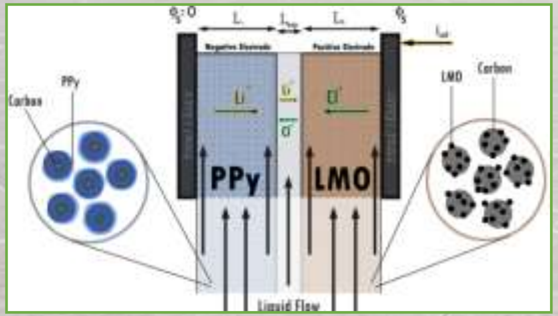




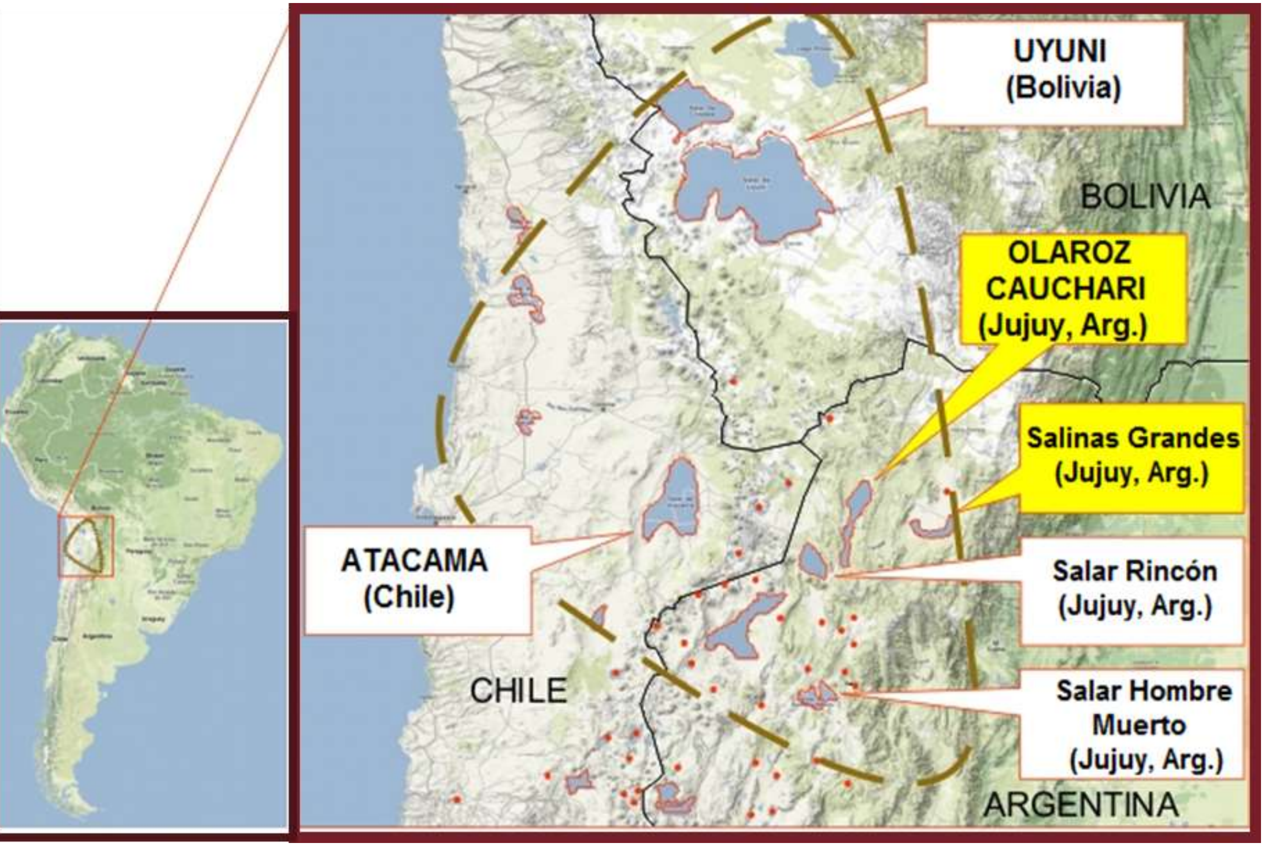
1,110 mA·h/g



Solar Energy Storage in an Electrochemical Reactor to Extract LiCl from Natural Brine



Largest lithium containing brines are in salt flats of South America

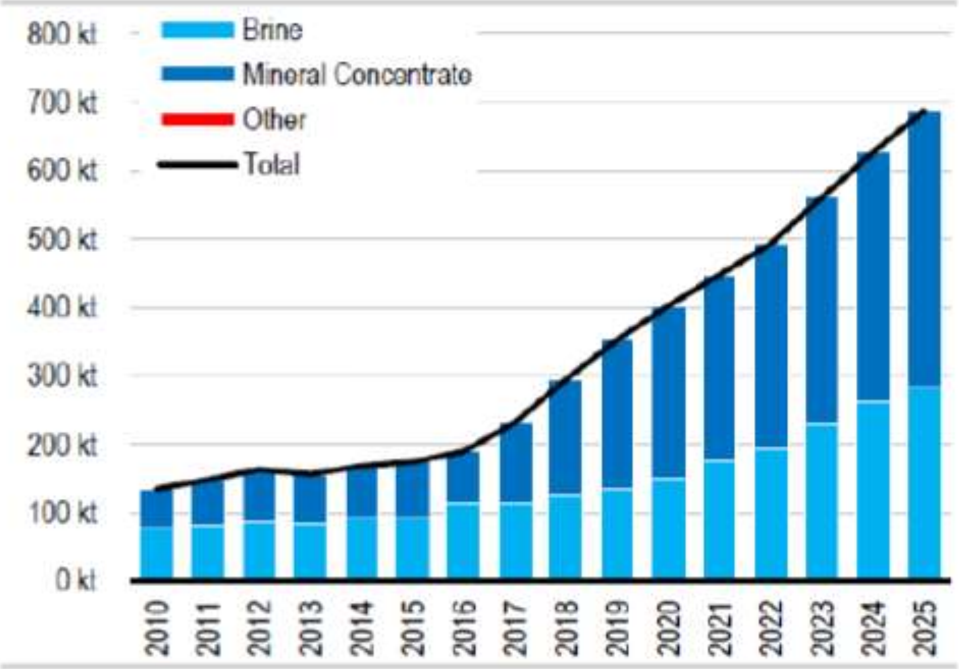


Salt flats at 4000 meters above sea level
65% of the world lithium reserves
80% of lithium containing brines

Argentina (Puna)
Bolivia (Uyuni)
Chile (Atacama)

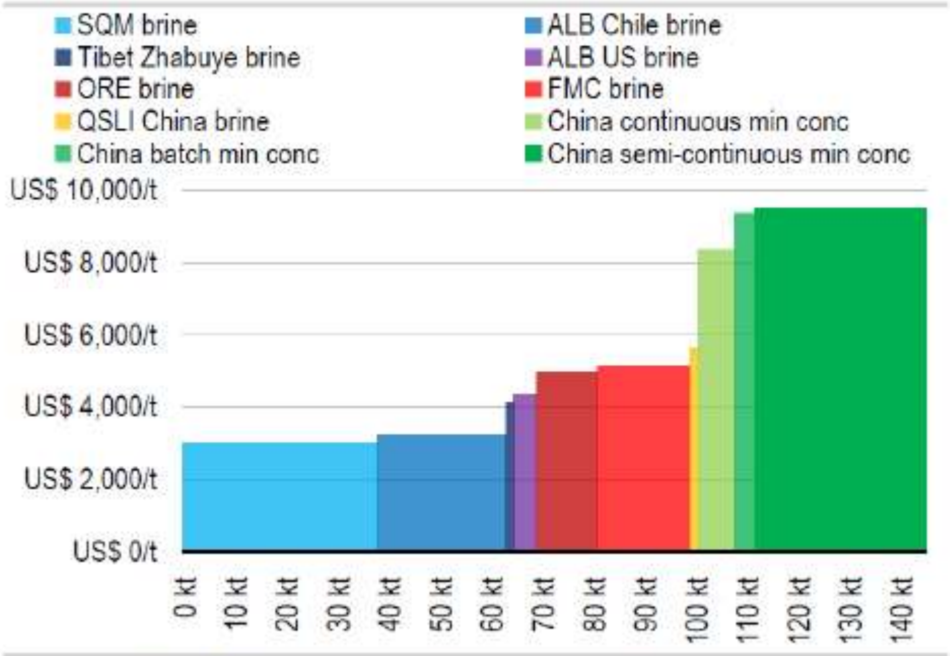
LITHIUM SUPPLY BY SOURCE

Historic and projected

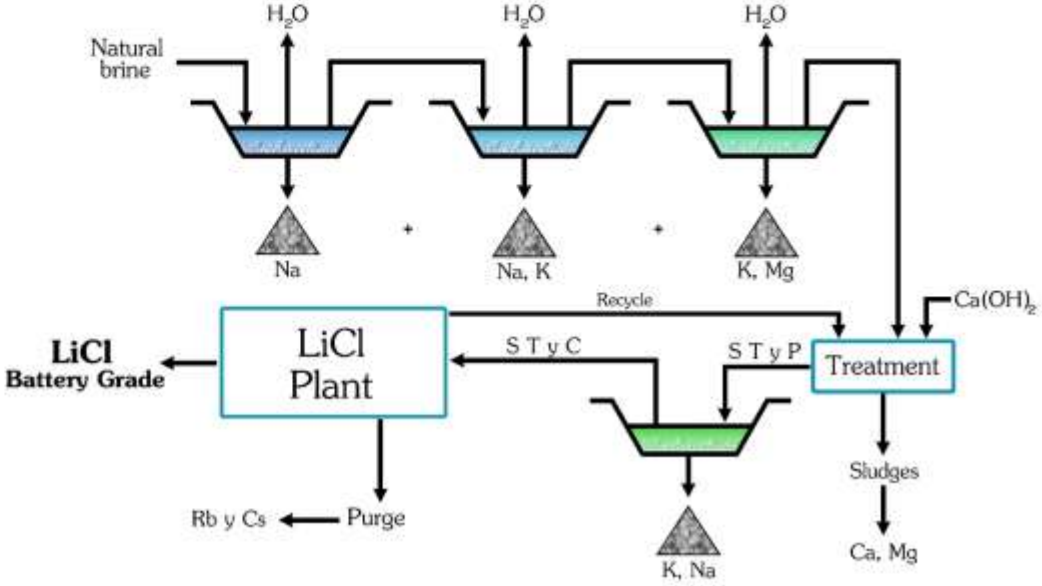


Source: Roskill, company reports, UBS estimates

LITHIUM PRODUCTION COSTS BY BY SOURCE



Source: Roskill, UBS NB: Brines are 2015 costs, mineral concentrate plants in China using 2017 spodumene contract prices.



Natural brine
H_2O
H_2O
H_2O
Na
Na, K
K, Mg
Recycle
$Ca(OH)_2$
LiCl Battery Grade
LiCl Plant
S T y C
S T y P
Treatment
Sludges
Rb y Cs
Purge
K, Na
Ca, Mg

CHEMICAL COMPOSITION OF BRINES FROM SALT FLATS

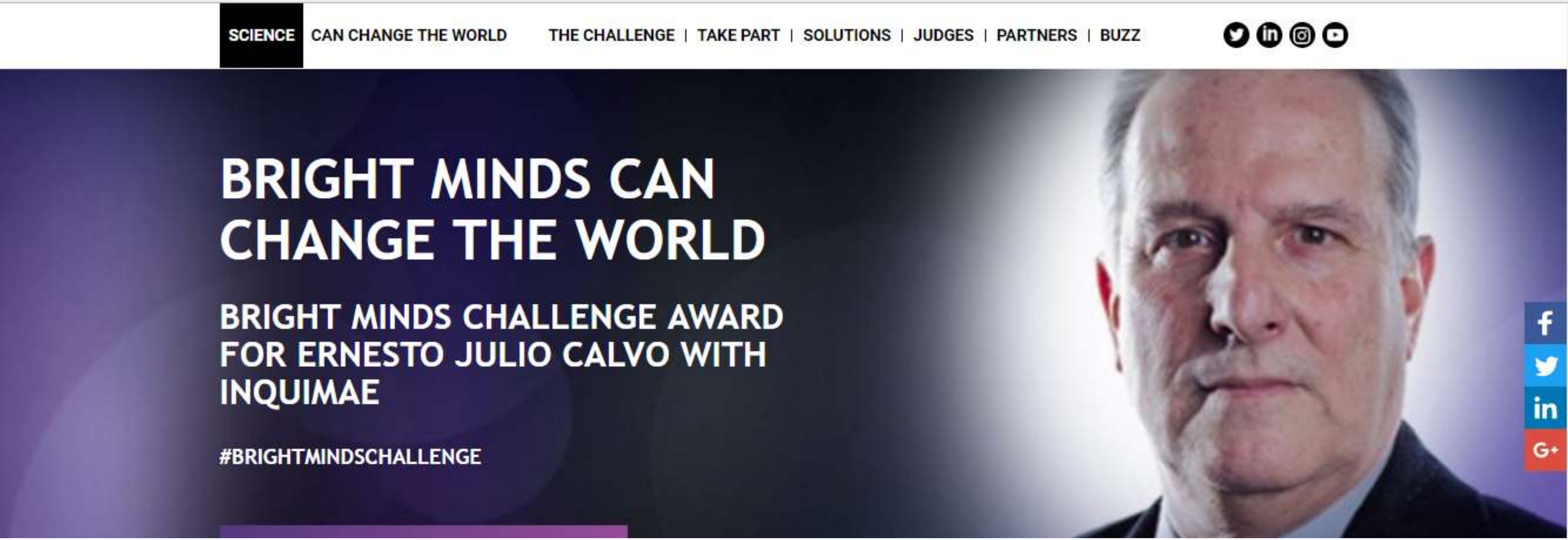
	Atacama	Uyuni	Hombre Muerto	Cauchari	Olaroz	Rincón
Na	7,60	8,75	9,79	9,55	9,46	9,46
K	1,85	2,72	0,617	0,47	0,656	0,66
Li	0,150	0,035	0,062	0,082	0,033	0,033
Mg	0,98	0,65	0,085	0,131	0,323	0,303
Ca	0,031	0,046	0,053	0,034	0,059	0,059
Cl	16,04	15,69	15,80	14,86	18,06	16,06
SO_4	1,65	0,85	0,853	1,62	1,015	1,015
B	0,064	0,020	0,035	0,076	0,040	0,040
K/Li	12,33	20,57	9,95	9,04	20,12	1,220
Na/Li	50,6	250	158	116	286	286
Mg/Li	6,53	18,6	1,37	2,52	9,78	9,29

Present Extraction Method

"Lime Soda" lithium extraction process from salt flat brine

very slow (8-12 months evaporation)
chemicals added (lime, solvay)
waste generation ($CaSO_4$, NaCl, $Mg(OH)_2$)
water loss (millions of gallons per ton)

Can we extract lithium at large scale in a sustainable way?

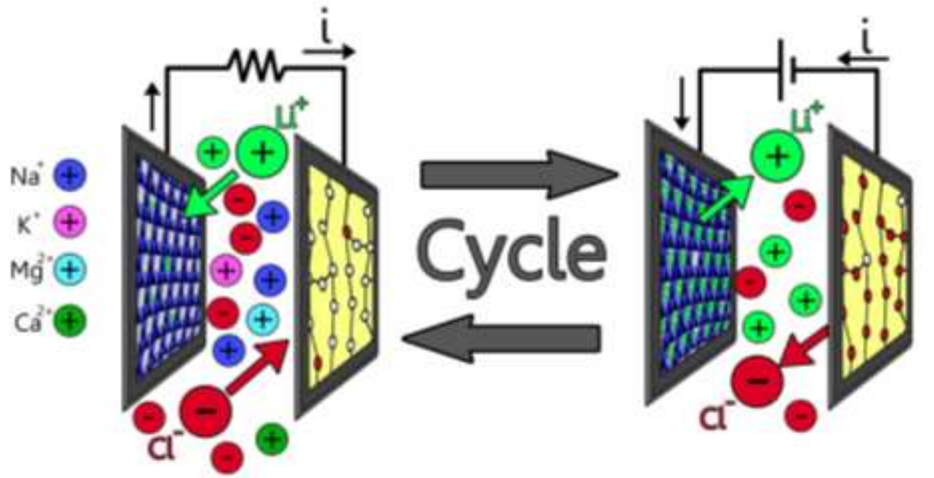


On 13 June 2017 scientist Ernesto Julio Calvo (Argentina), who invented [Inquimae] - a new way of extracting lithium that is powered by solar energy and is quicker and cleaner than any existing technology - won the first prize in the Bright Minds Challenge. He will be awarded with 500 hours expert support to accelerate the scaling-up of his solution from DSM and its partners. The prize was handed over by DSM CEO Feike Sijbesma at an award ceremony during the Bright Minds Challenge Grand Final in Amsterdam, the Netherlands

Solar Energy Storage in an Electrochemical Reactor to Extract LiCl from Natural Brine

Two step electrochemical process

1. Extraction from Brine **2. Recovery in dilute electrolyte**



Battery generates energy Consumes energy

A LiMn2O4-Polypyrrole System for the Extraction of LiCl from Natural Brine, L.L. Missoni, F. Marchini, M. del Pozo, E.J. Calvo, J. Electrochem. Soc., **163** (9) A1898-A1902 (2016).

E.J. Calvo, F. Marchini, WO 2014/047347 A1, Low impact Lithium Recovery from aqueous solutions

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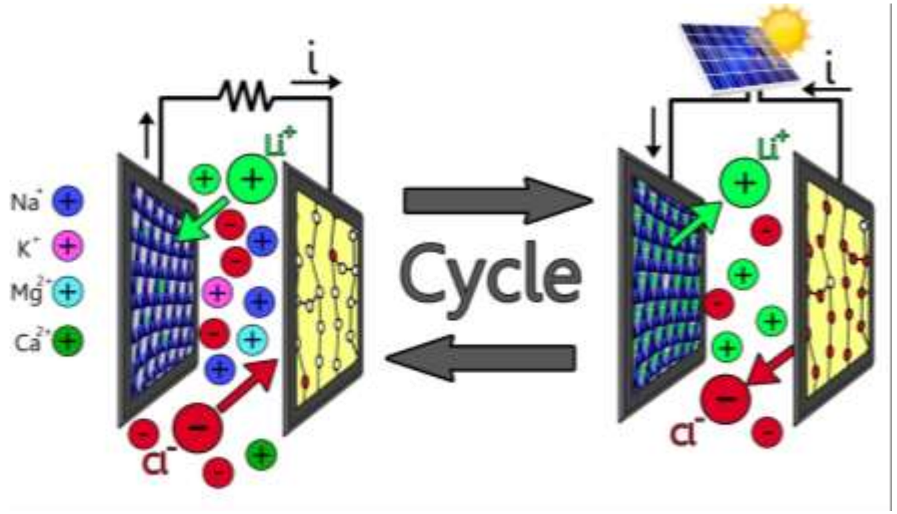

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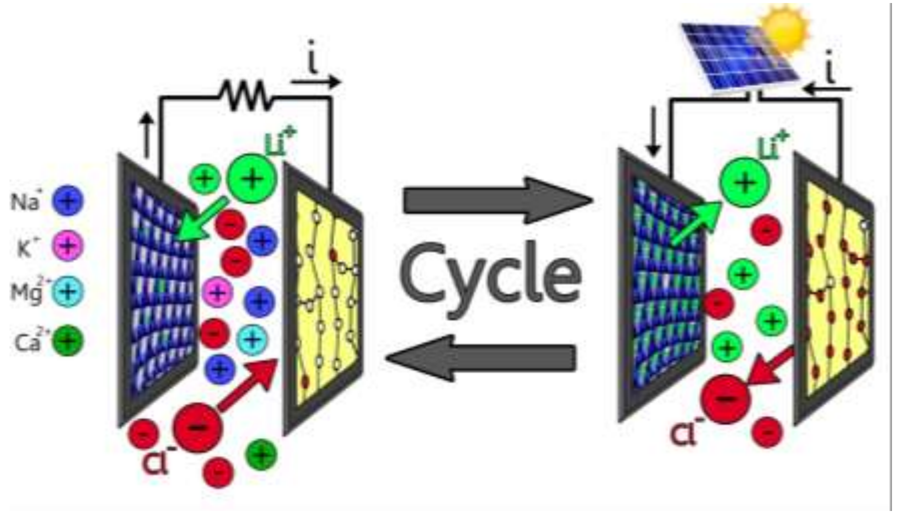
E.J. Calvo, F. Marchini, WO 2014/047347 A1, Low impact Lithium Recovery from aqueous solutions

OUR SOLUTION

Two step electrochemical process

1. Extraction from Brine **2. Recovery in dilute electrolyte**



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E.J. Calvo, F. Marchini, WO 2014/047347 A1, Low impact Lithium Recovery from aqueous solutions

What is unique?

- **Fast**
- **Environmentally Friendly**
- **Low Energy Cost**
- **Highly Selective for lithium**

Premium Solar energy

↓

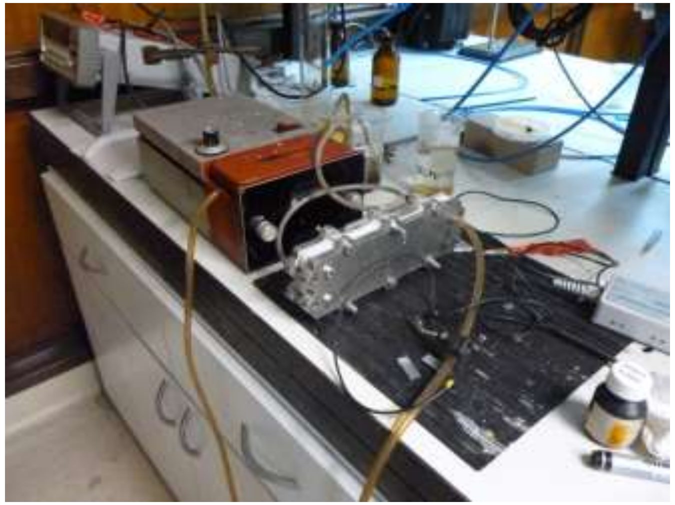
Extract lithium chloride

↓

Lithium batteries

↓

Intermittent renewable energy storage

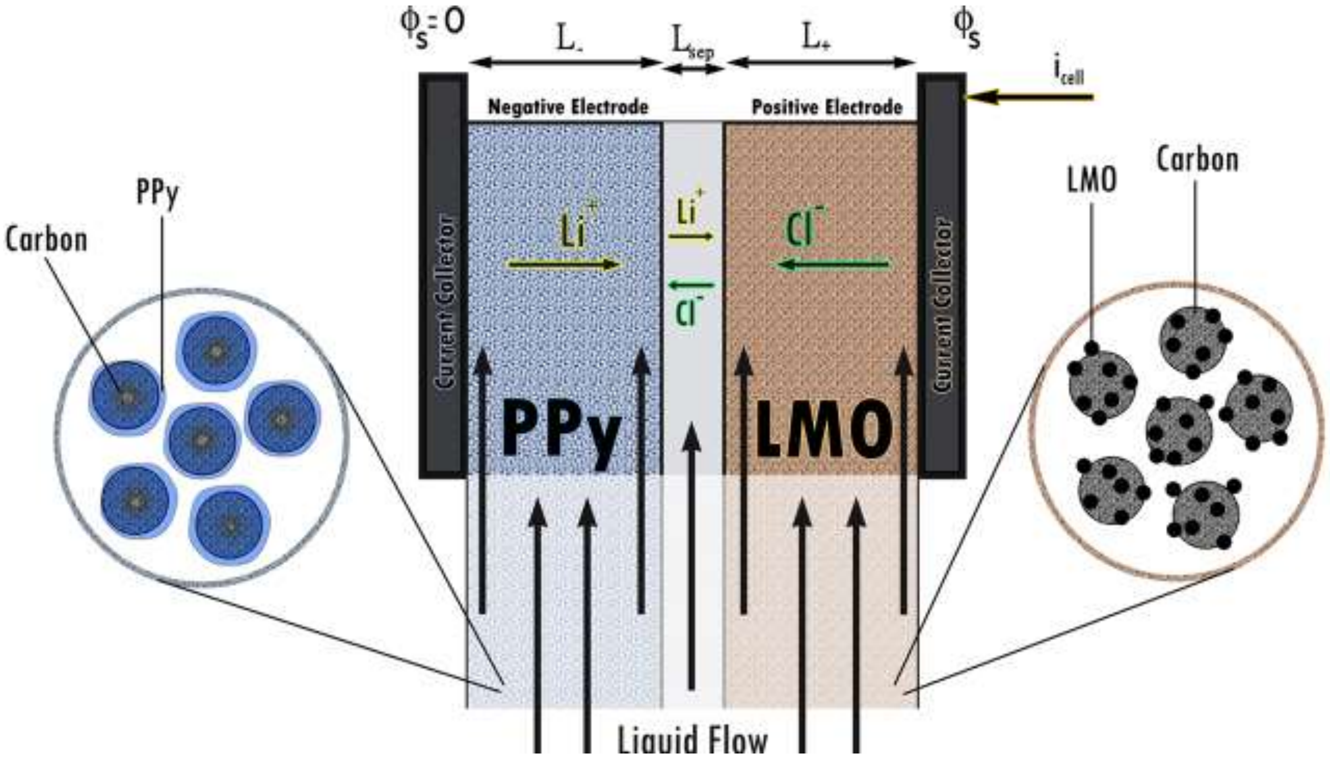


ELECTROCHEMICAL REACTOR

$Li_{1-x}Mn_2O_4$ (LMO) LITHIUM-ION POROUS ELECTRODE

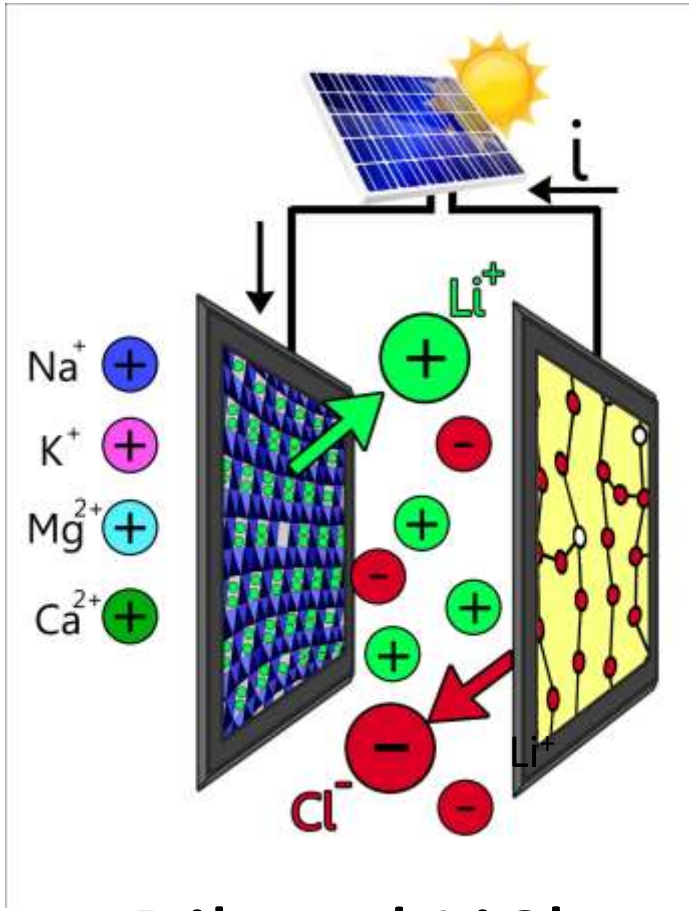
POLYPYRROLE (PPy) CHLORIDE SELECTIVE SUPERCAPACITOR POROUS ELECTRODE

ELECTROLYTE SEPARATOR

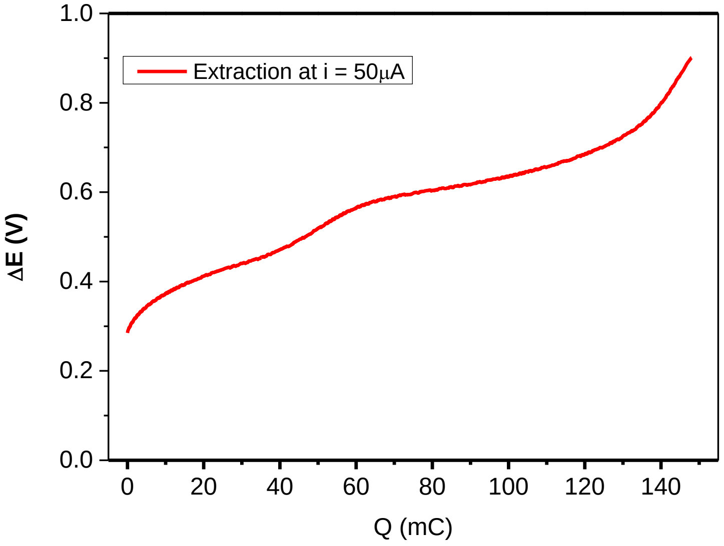


We store solar energy in a battery-reactor to extract lithium chloride from Natural Brine

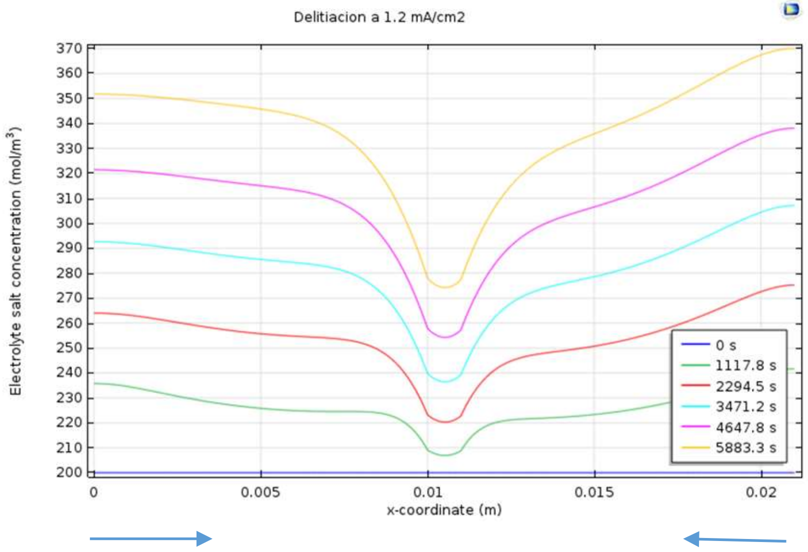
Battery charge from Solar Energy



Diluted LiCl



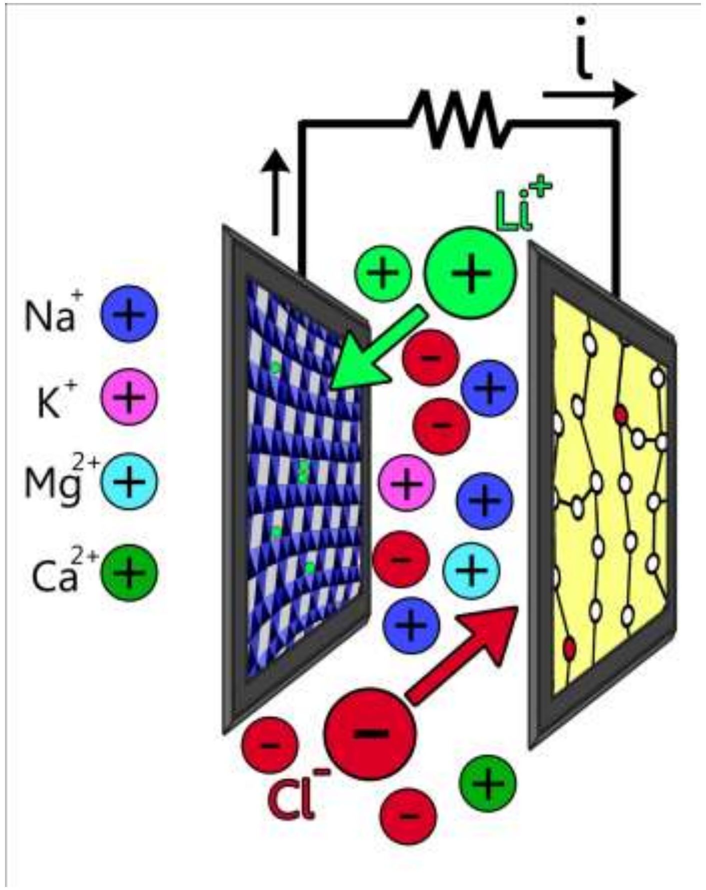
LiCl RECOVERY



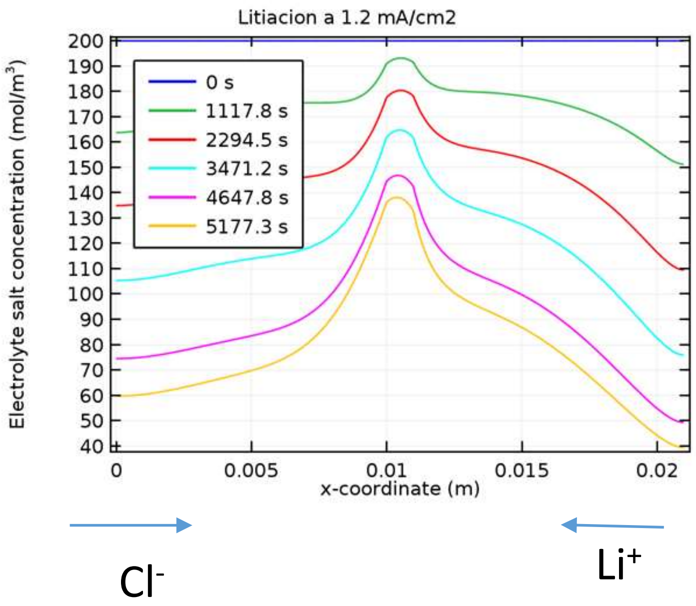
Cl^- Li^+

Dicharge of battery-reactor in Natural Brine to extract Lithium Chloride

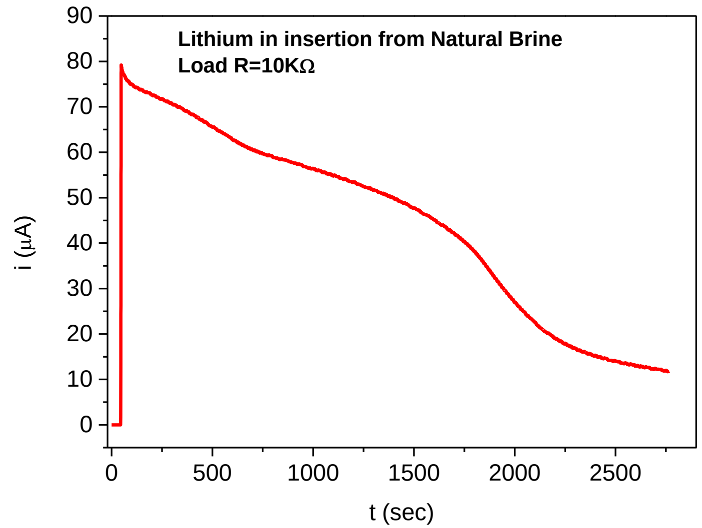
Spontaneous Process

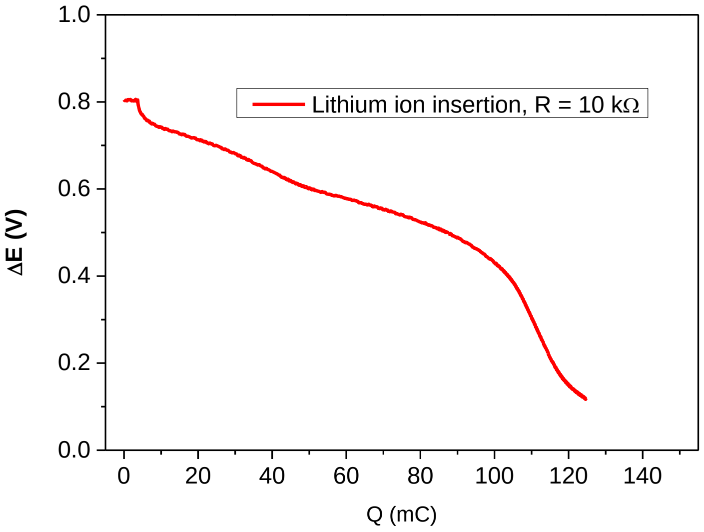


Brine

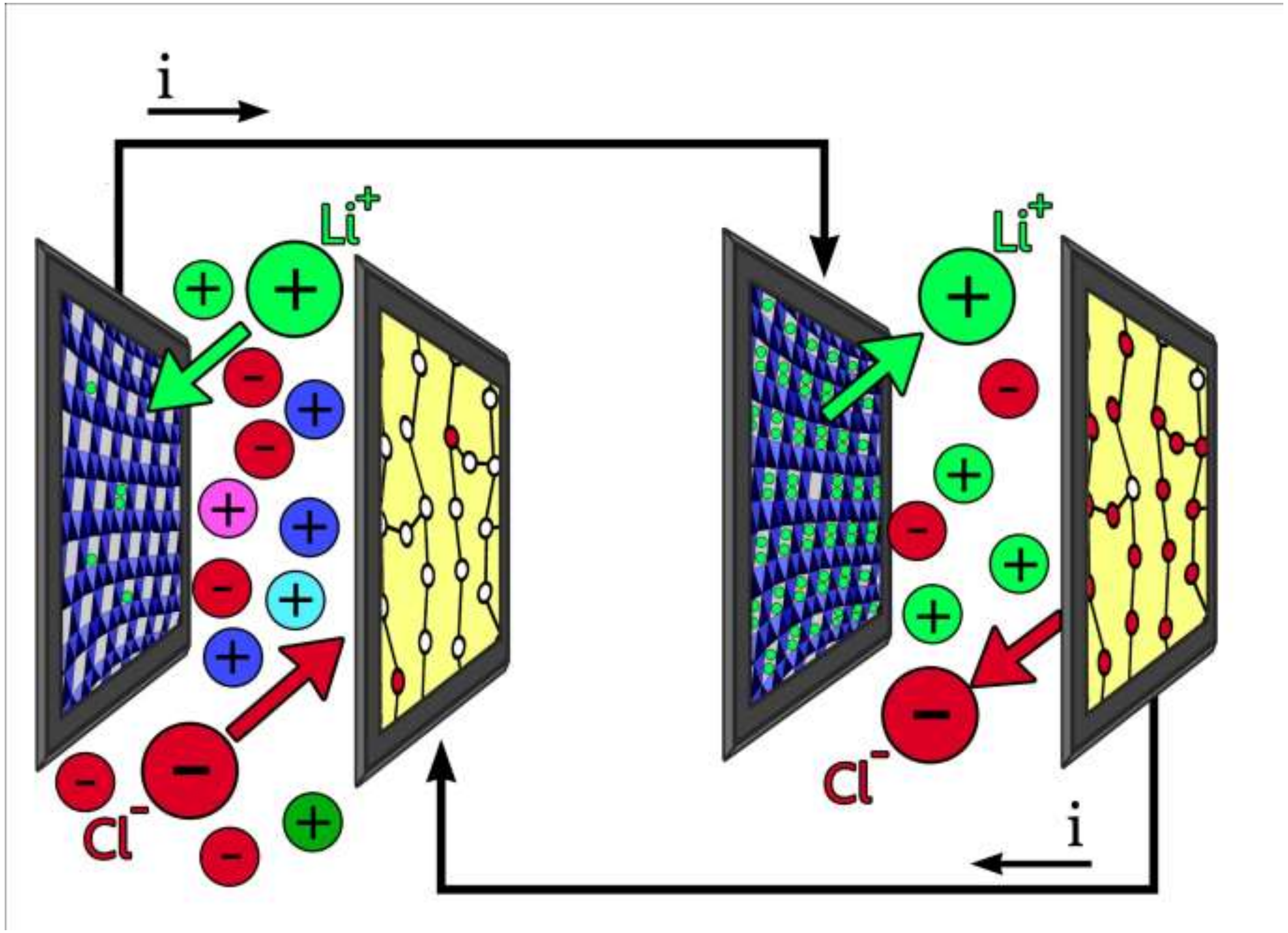


LiCl EXTRACTION

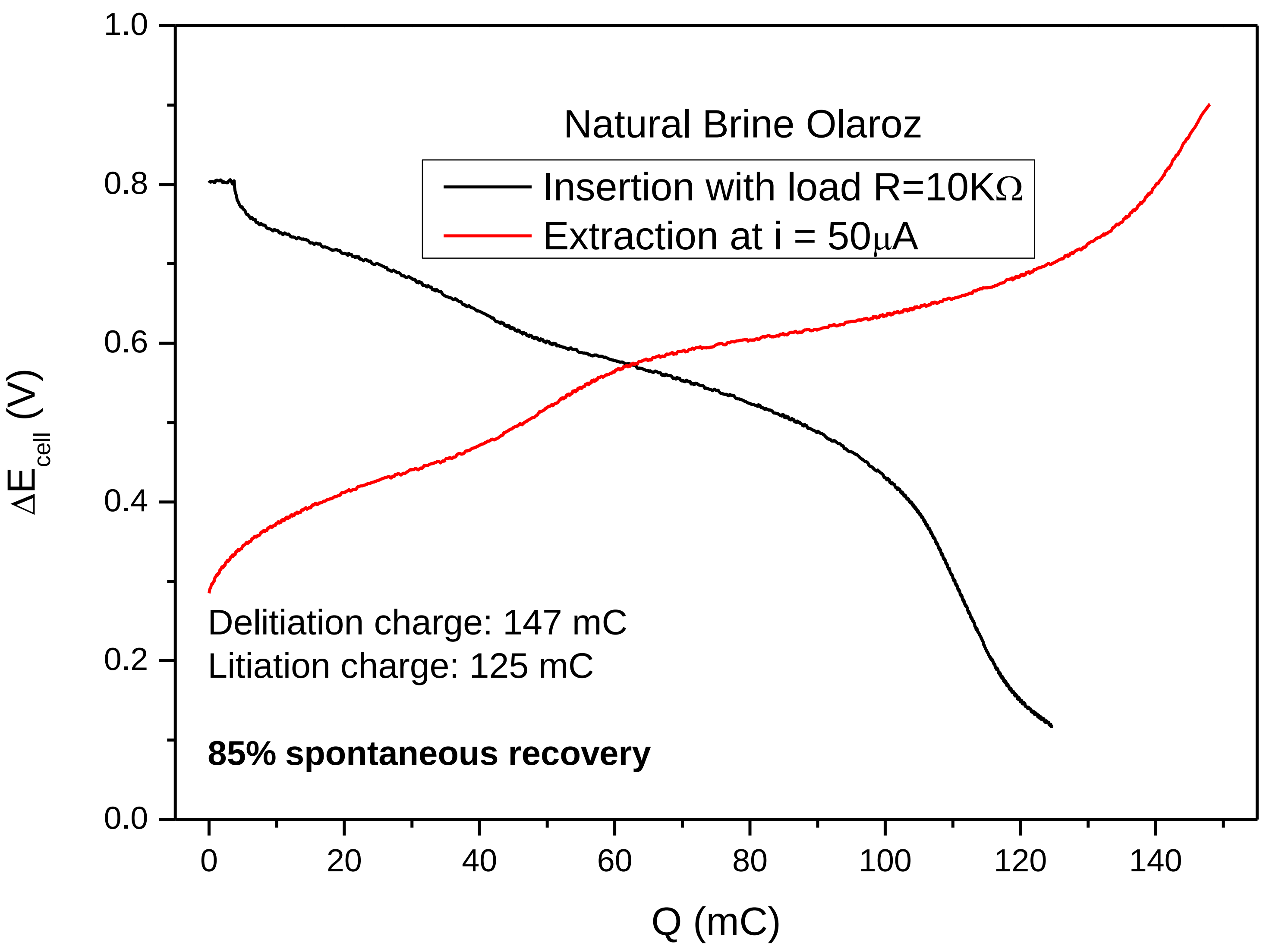




The spontaneous process on the left side (capture of LiCl from natural brine) feeds electrical charge into the right side reactor (release of LiCl)



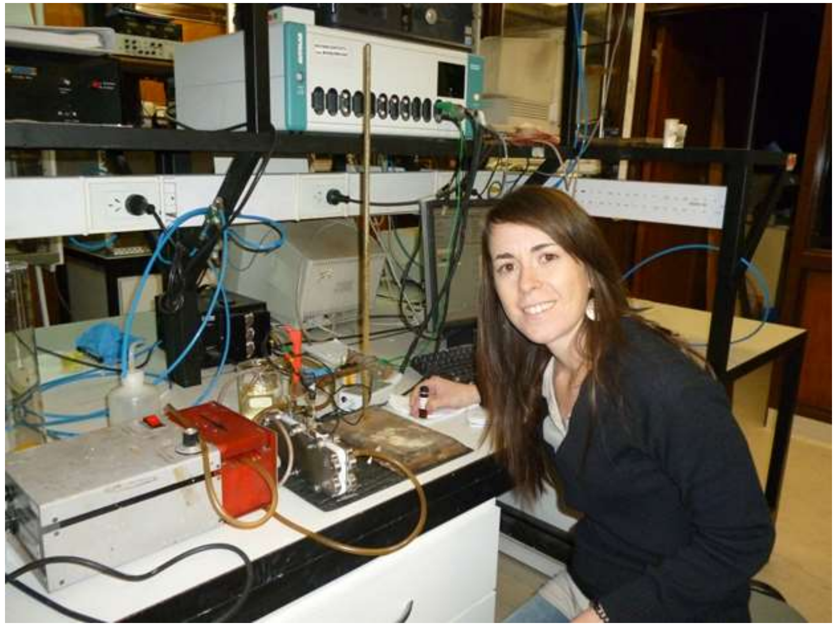
BRINE **DILUTED LiCl**

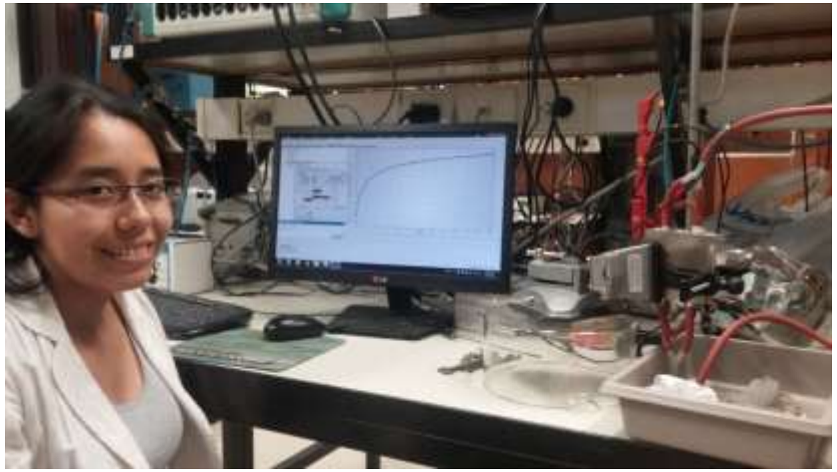

Natural Brine Olaroz
Insertion with load R=10KΩ
Extraction at i = 50μA
Delitiation charge: 147 mC
Litiation charge: 125 mC
85% spontaneous recovery
ΔE_cell (V)
Q (mC)
0.0
0.2
0.4
0.6
0.8
1.0
0
20
40
60
80
100
120
140

SUCCESFUL PROOF OF CONCEPT

Scientific and technology activities at the new lithium research center in Jujuy, Argentina will attract PhD students and young researchers worldwide.

Environmental advantage to preserve a pristine environment: Electrochemistry is a clean technology





Extra bonus: Can we also fix CO_2 from the atmosphere into lithium carbonate?

WHERE ARE WE?

Basic Science

Design of Electrochemical Method

Proof of Concept Validated & patents

Lithium Research Center

Bench Top Modelling

Electrochemical Engineering

Unit Process

WHERE WE WANT TO GO?

NEXT STEP

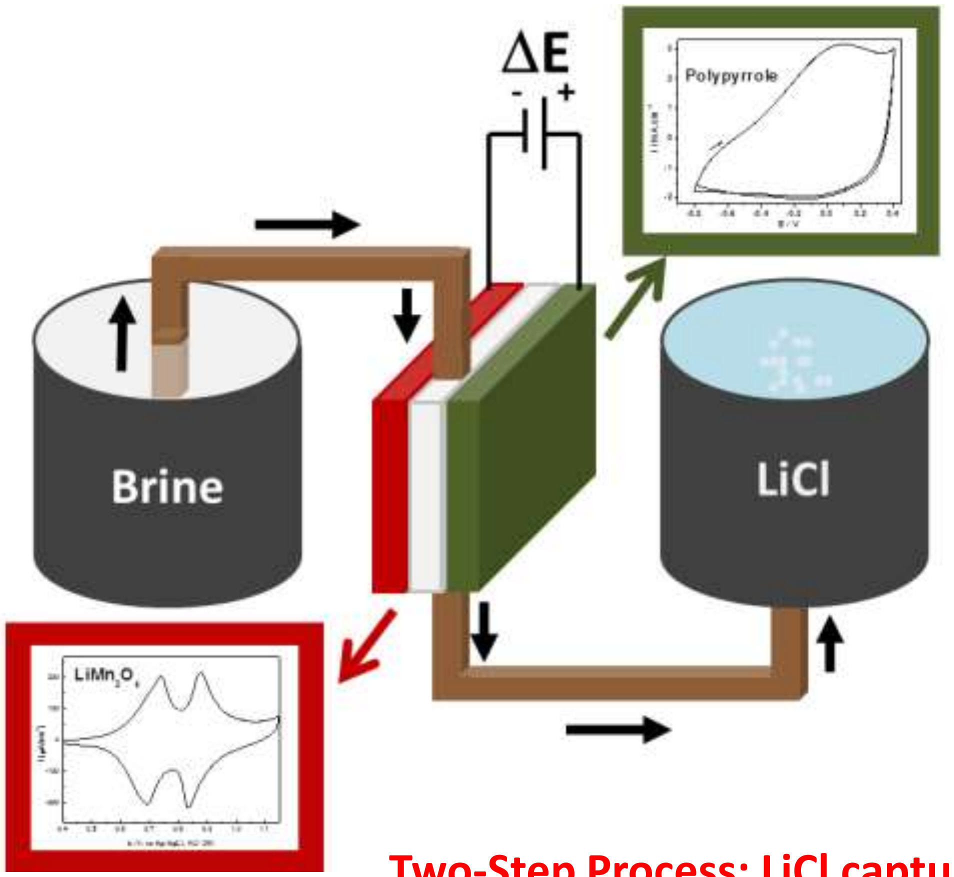
Small self –contained mobile demonstration pilot plant at 4000 meters above sea level in the salt flat to scale up to an industrial process from brine to lithium salts

A1898 Journal of The Electrochemical Society, 163 (9) A1898-A1902 (2016)
0013-4651/2016/163(9)/A1898/5/$33.00 © The Electrochemical Society

A $LiMn_2O_4$-Polypyrrole System for the Extraction of LiCl from Natural Brine

Leandro L. Missoni, Florencia Marchini, María del Pozo, and Ernesto J. Calvo[z]

INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, AR-1428 Buenos Aires, Argentina



CATHODE Selective to Lithium

$$xLi^+(brine) + Li_{1-x}Mn^{III}_{1-X}Mn^{IV}O_2 + xe^-(cathode) \leftrightharpoons LiMn^{IV}Mn^{III}O_4$$

ANODE Selective to Chloride

$$xCl^-(brine) + xPP^o(anode) \rightleftharpoons x[PP^+Cl^-] + xe^-(anode)$$

OVERALL REACTION

$$xLi^+(brine) + xCl^-(brine) + Li_{1-x}Mn^{III}_{1-X}Mn^{IV}O_2 + xPP^0 \leftrightharpoons LiMn^{IV}Mn^{III}O_4 + x[PP^+Cl^-]$$

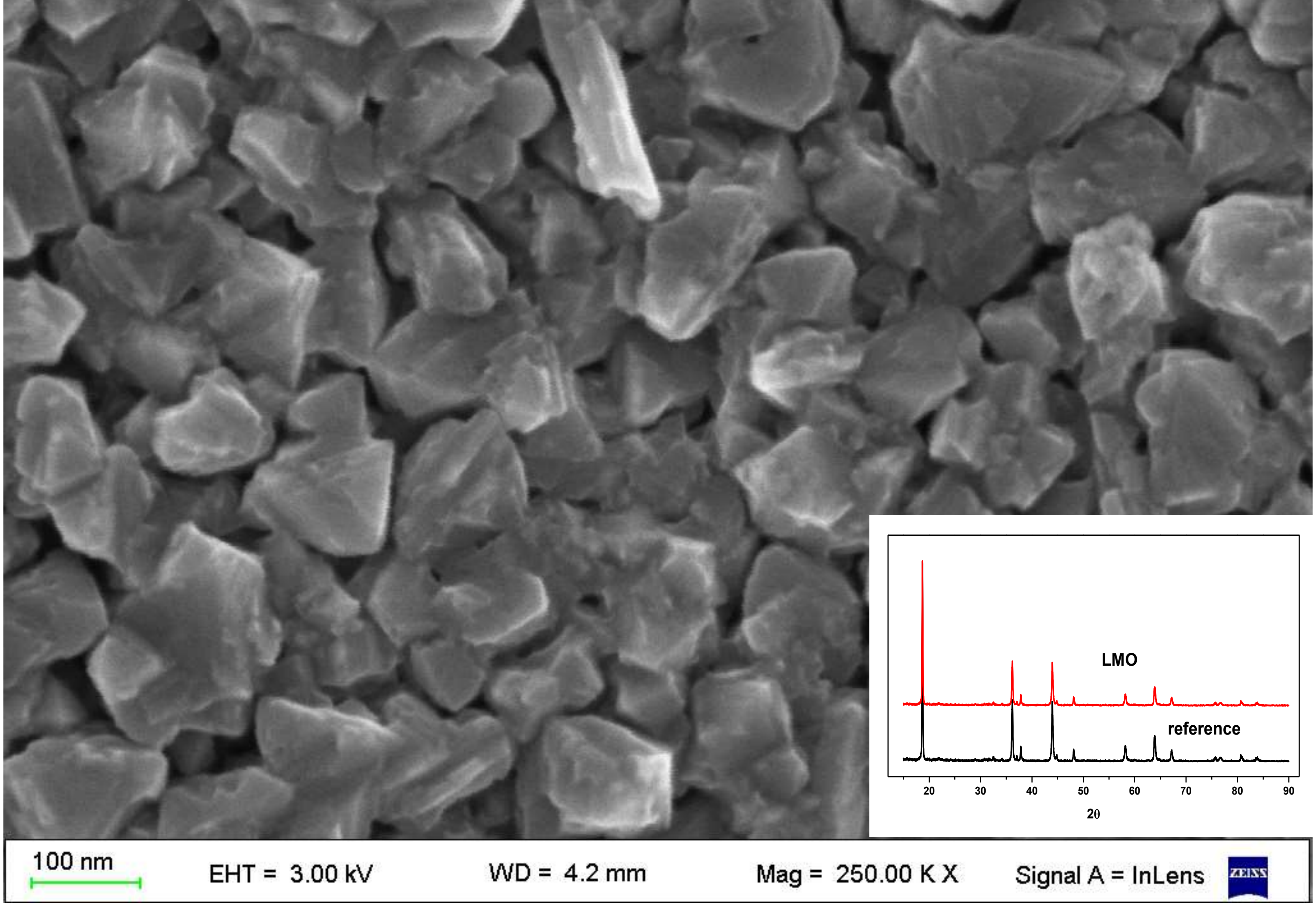
By limiting the potential we avoid the reaction:

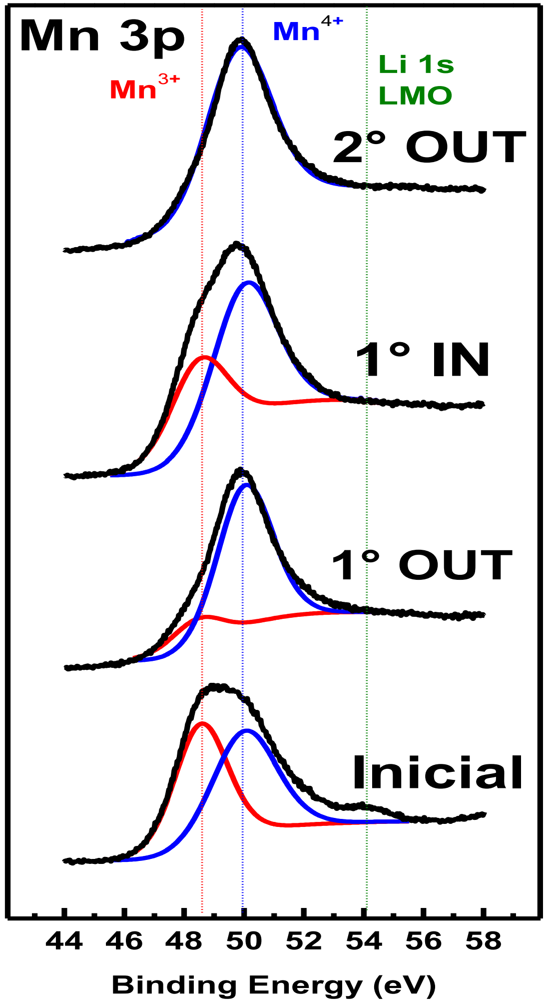
$$LiMn^{IV}Mn^{III}O_4 + xLi^+ + xe \rightleftharpoons Li_{1+x}Mn^{III}_{1+x}Mn^{IV}_{1-x}O_4$$

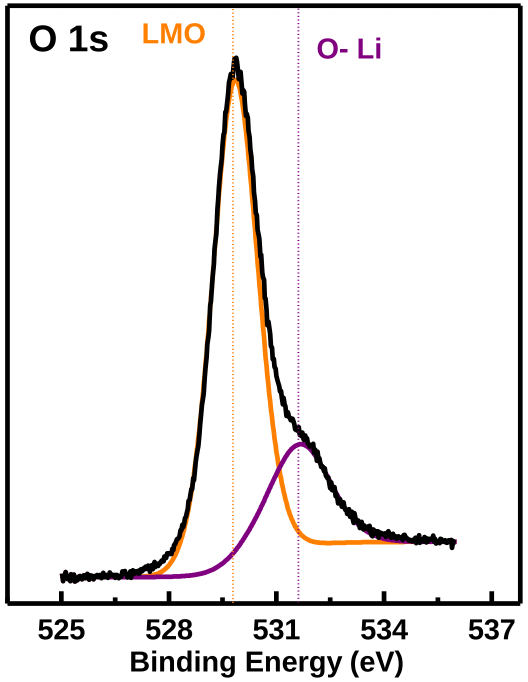
With two phase $LiMn_2O_4$ / $Li_2Mn_2O_4$ separation

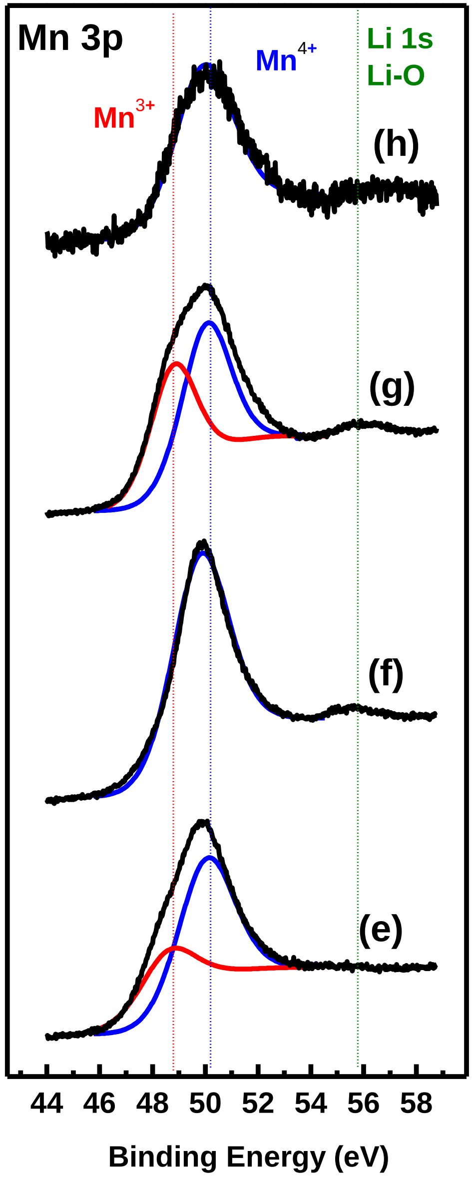
Two-Step Process: LiCl capture and recovery

Pld deposited film

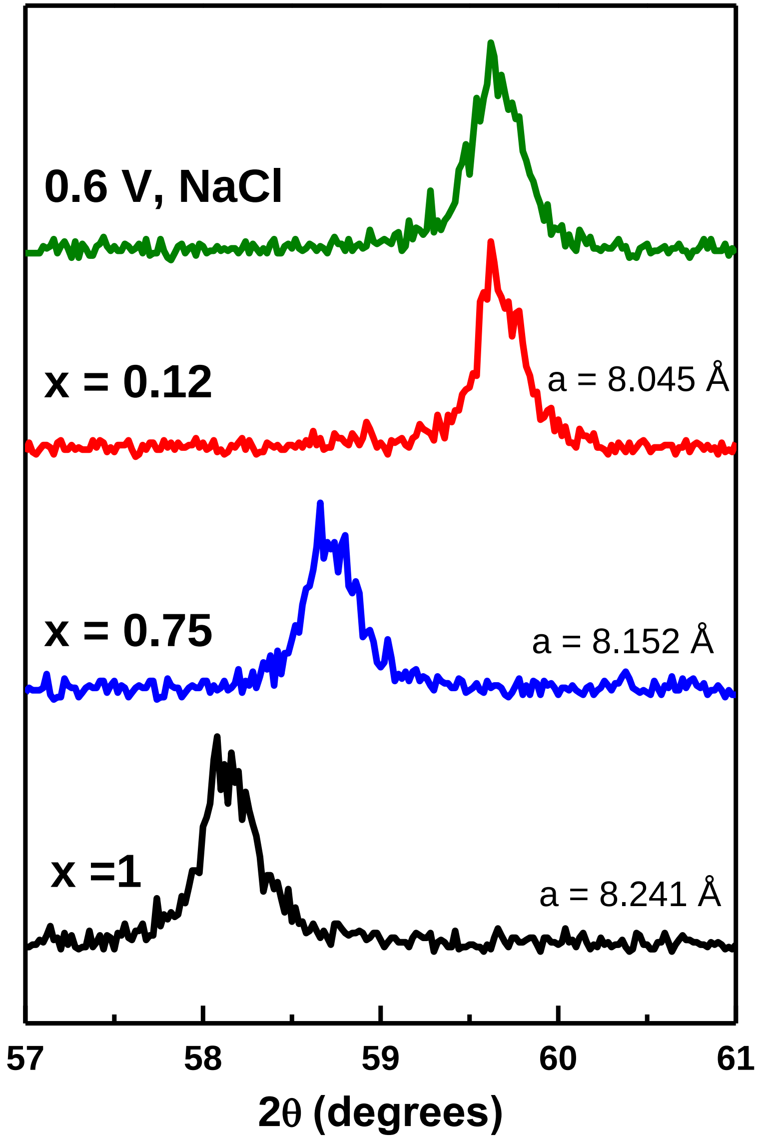




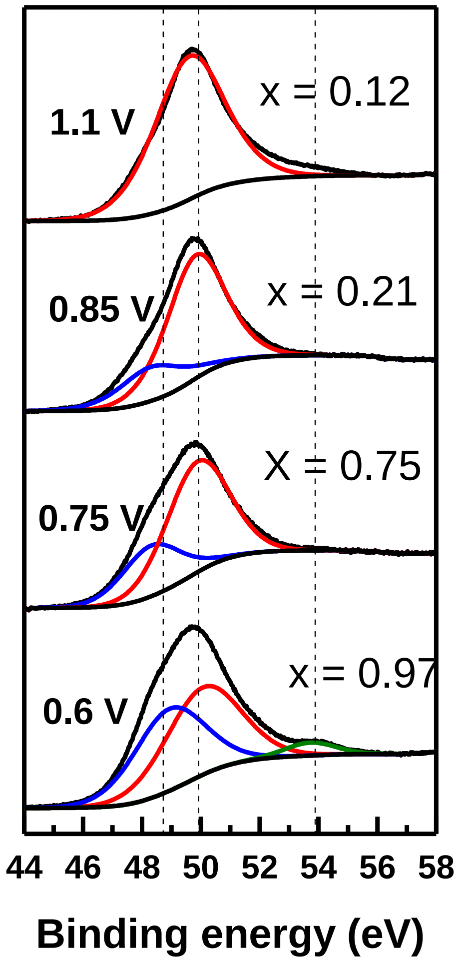


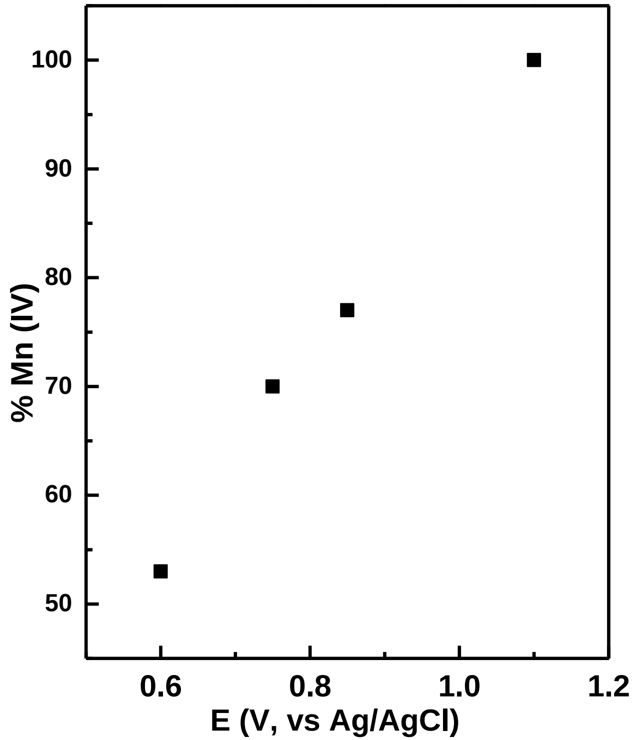


e) 2nd. insertion in 0.1 M LiNO3 + 0.1 M NaNO3 (12 mC.cm-2);
f) 3rd. extraction (71 mC.cm-2);
g) 3rd. insertion in 0.1 M LiNO3 and 1 M NaNO3 (48 mC.cm-2);
h) MnO2 reference signal.



BULK CRYSTAL XRD





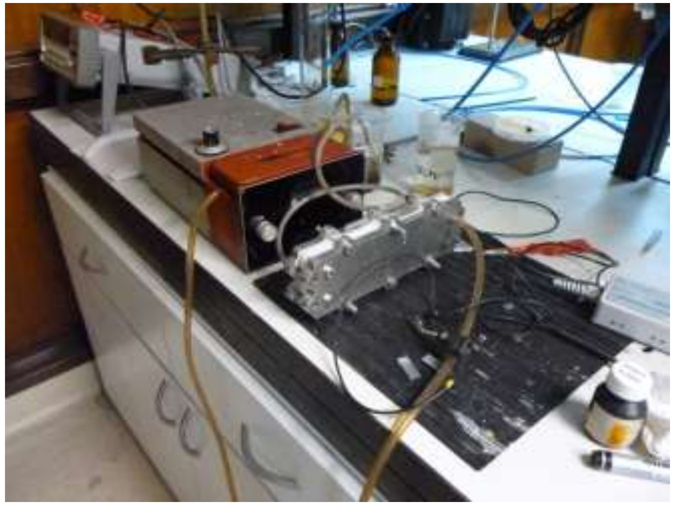
SURFACE XPS ANALYSIS

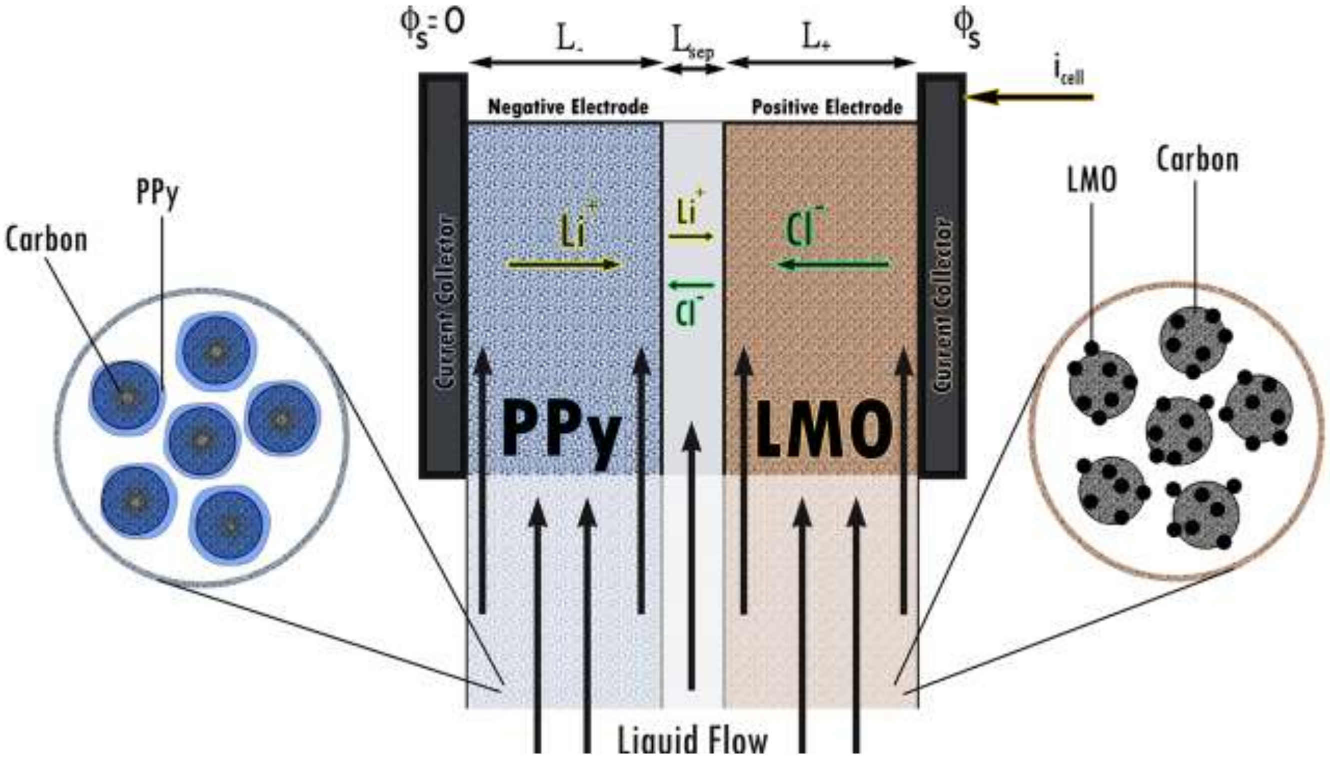
ELECTROCHEMICAL REACTOR

$Li_{1-x}Mn_2O_4$ (LMO) LITHIUM-ION POROUS ELECTRODE

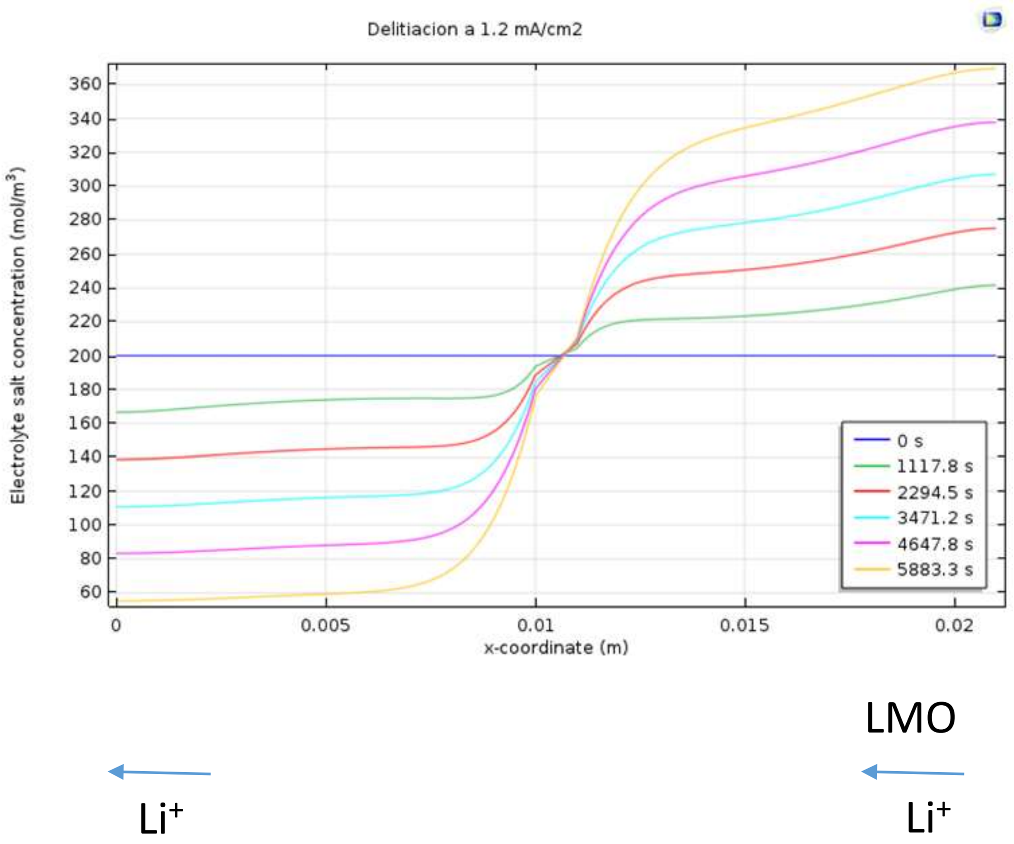
POLYPYRROLE (PPy) CHLORIDE SELECTIVE SUPERCAPACITOR POROUS ELECTRODE

ELECTROLYTE SEPARATOR

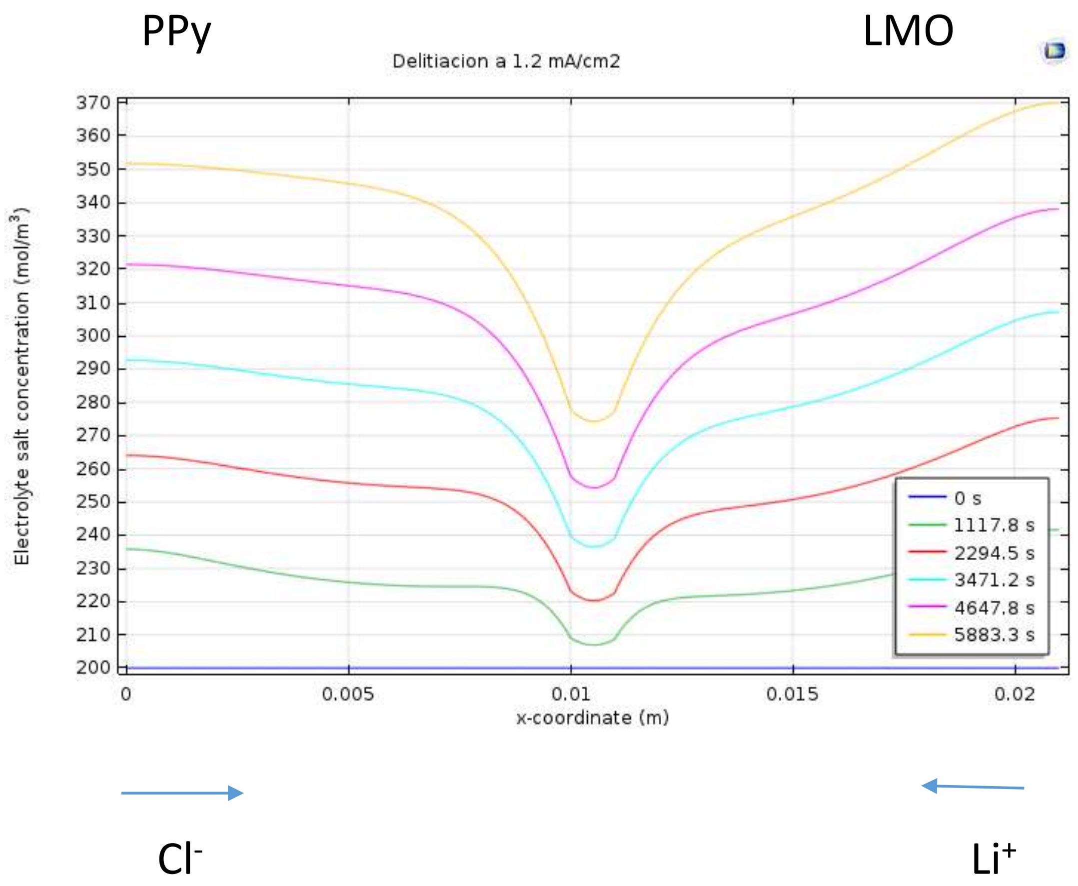




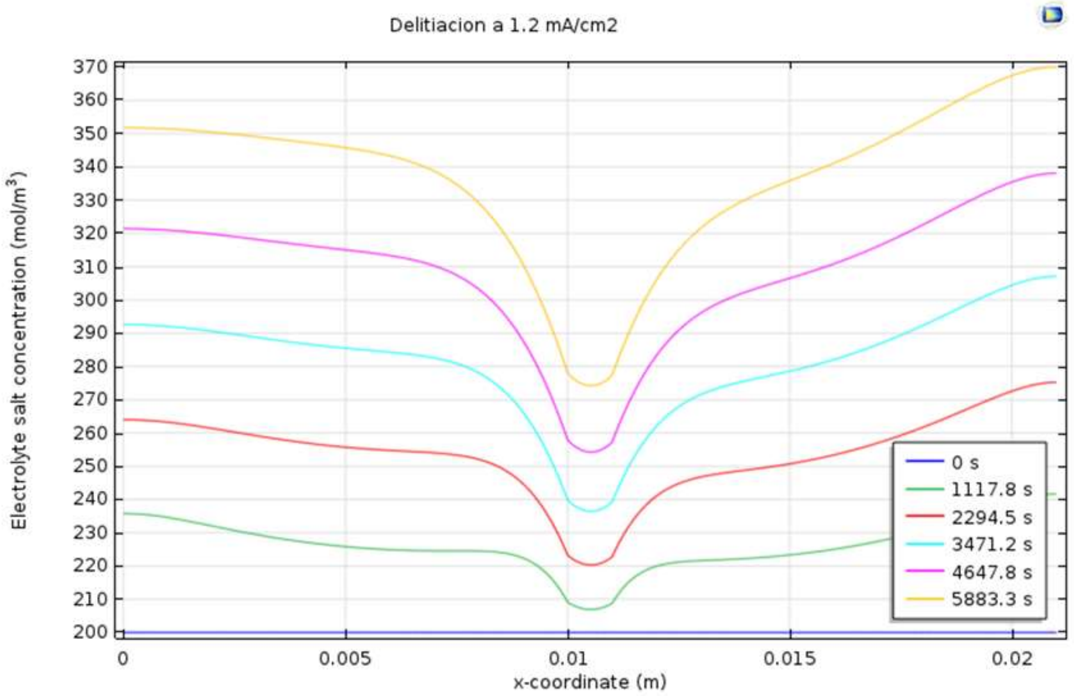
DOUBLE LAYER ASSYMETRIC CAPACITOR



POLYPYRROLE ASSYMETRIC CAPACITOR

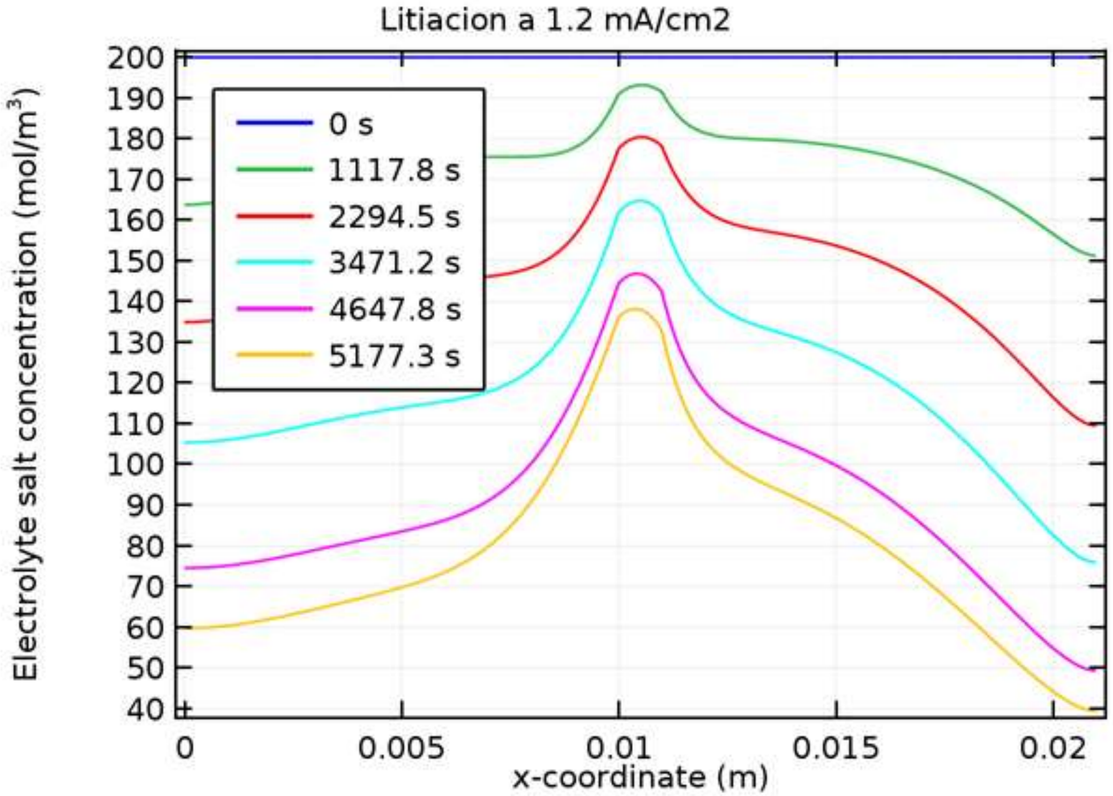


PPY-LMO HYBRID ASSYMETRIC LITHIUM ION CHLORIDE SELECTIVE SUPERCAPACITOR
Two-Step Process: LiCl capture and recovery



Cl^- Li^+

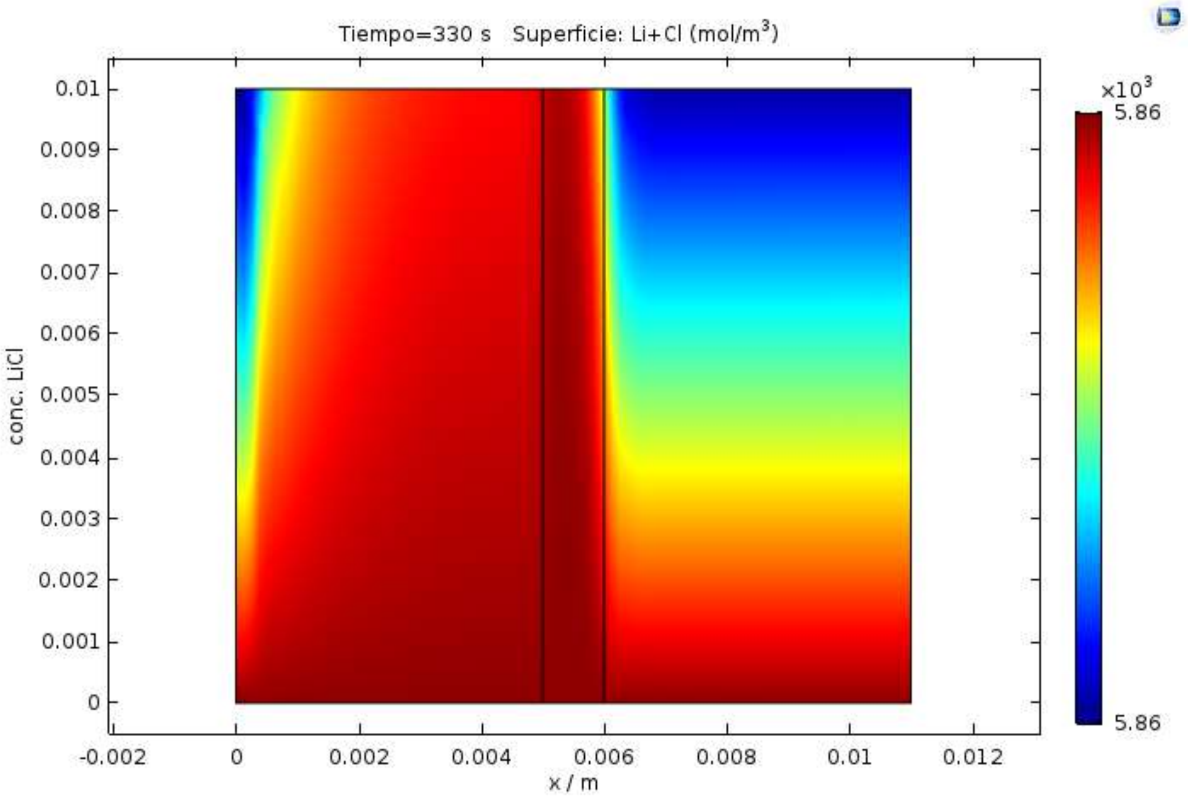
LiCl RECOVERY

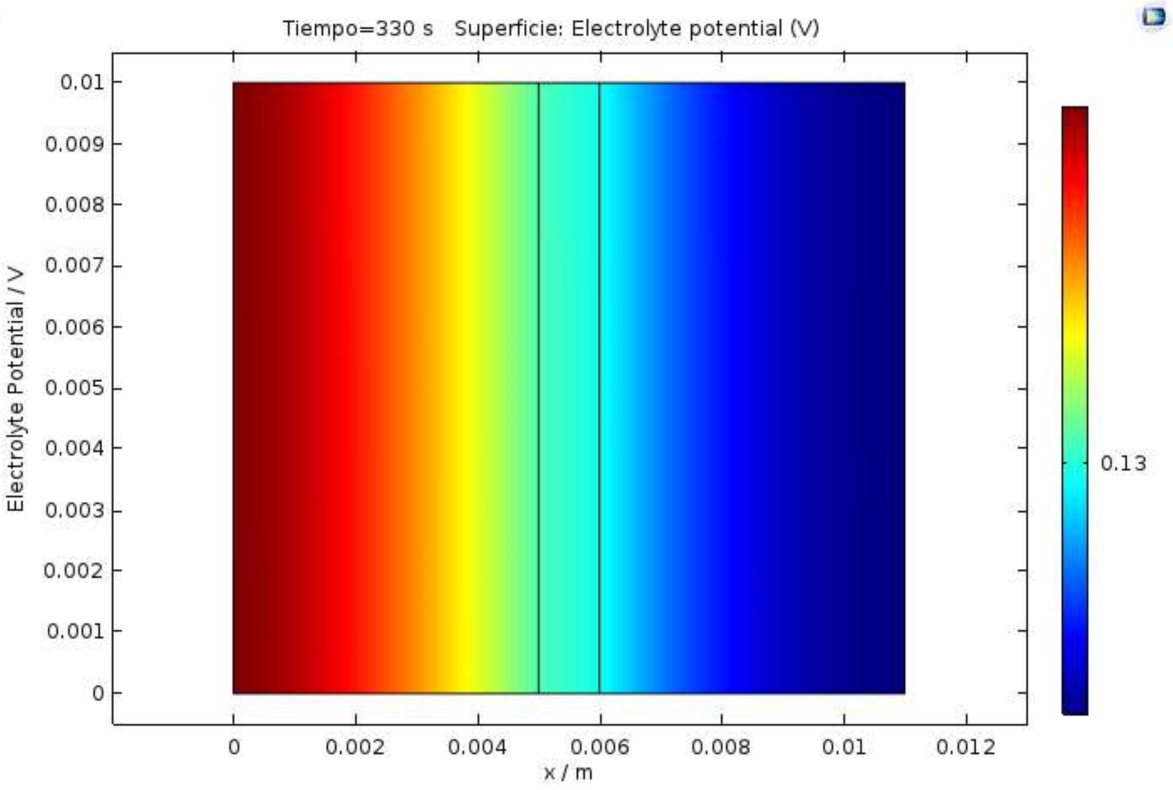


Cl^- Li^+

LiCl EXTRACTION

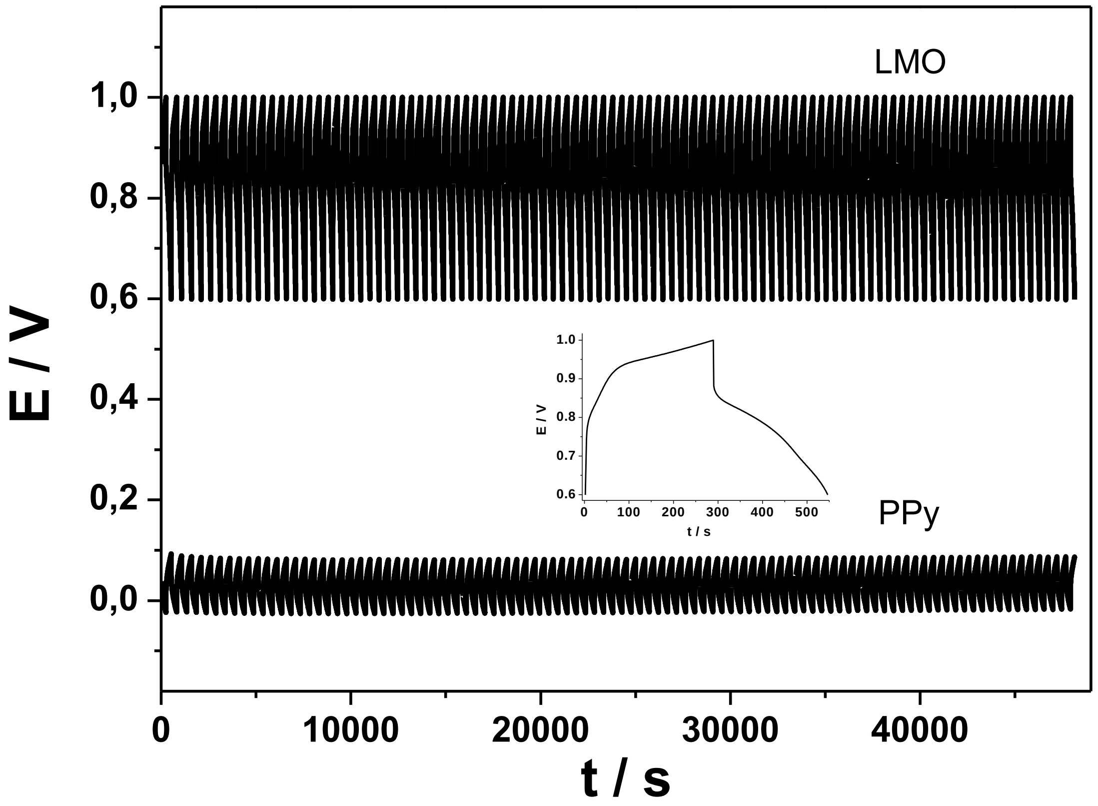
SIMULATION OF 2D BATTERY-REACTOR DURING LITHIUM INSERTION





3 x 10^4 m/s
50 A/ m^2

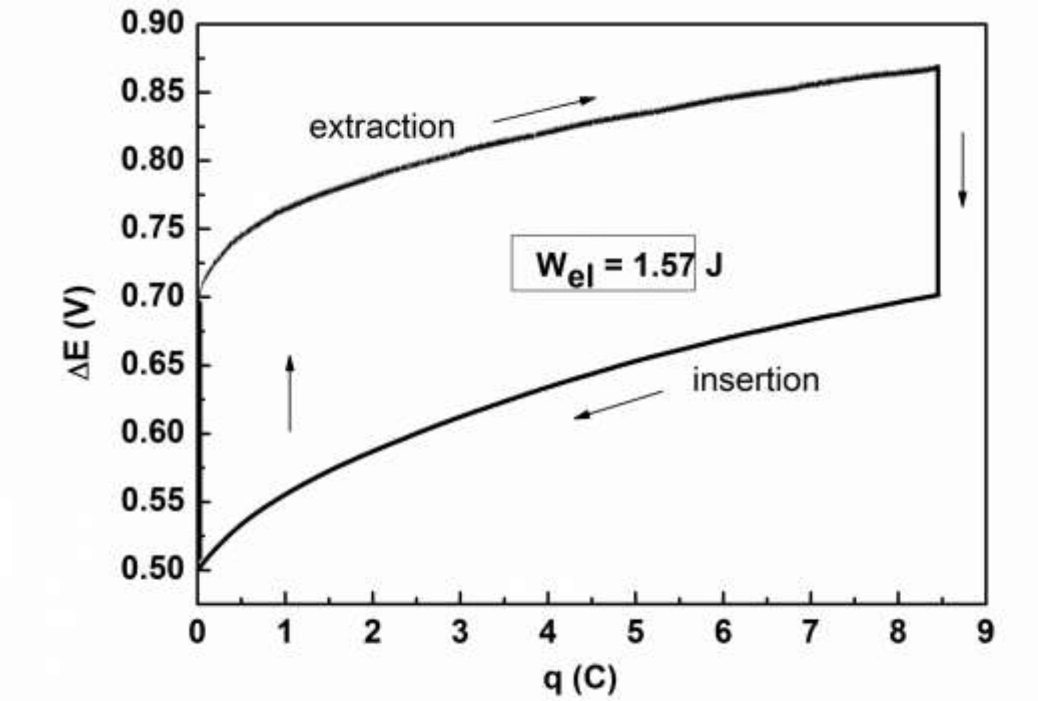
STABILITY OVER 200 CYCLES



Q (C)	Li^+ (mg)	$Li^+_{(exp)}$ (mg)	Efficiency (%)
42.8	3.10	1.73	56
57.5	4.17	2.23	53
61.2	4.43	2.01	45

ENERGY BALANCE

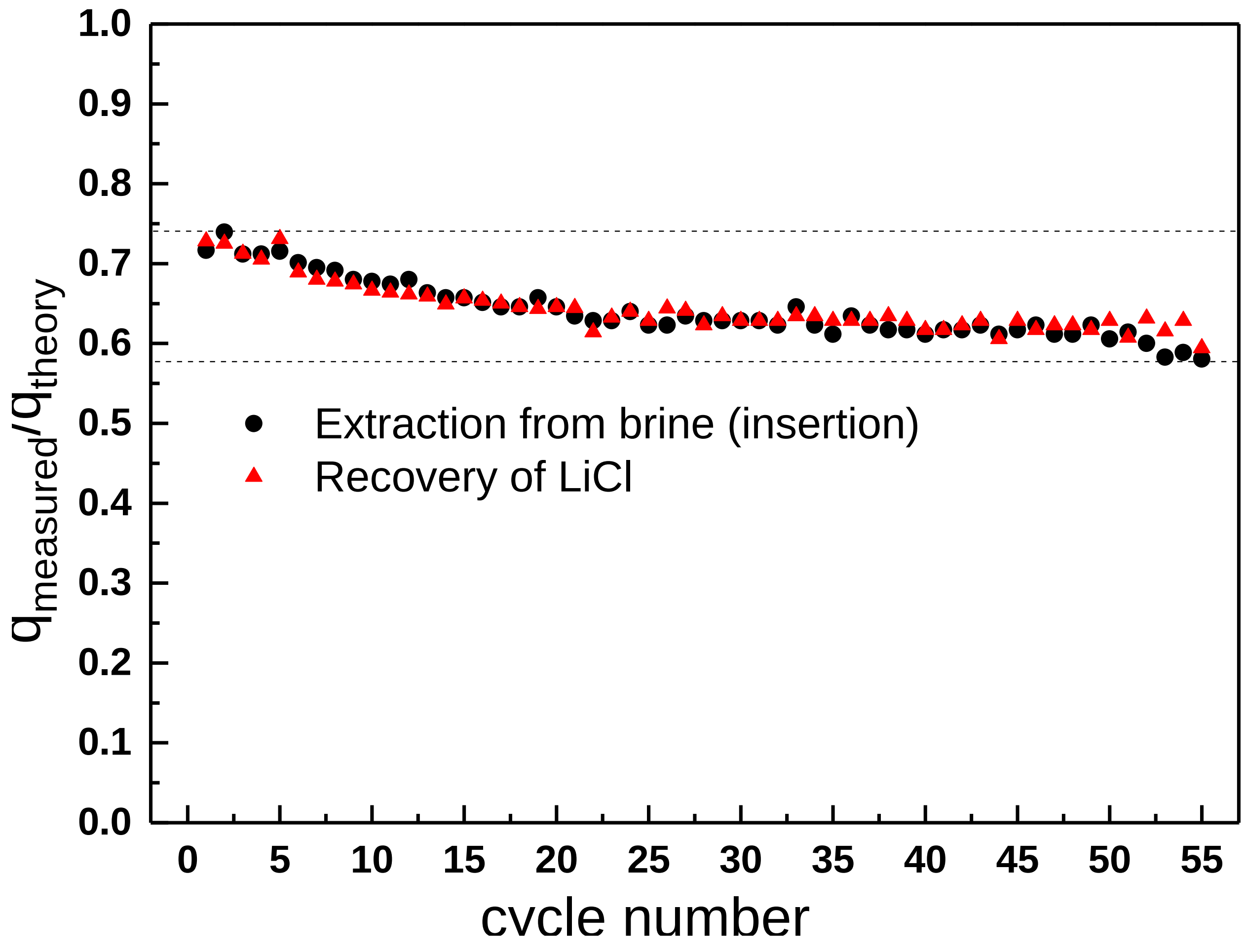
$$W = \oint_C \Delta E . dq$$



10 Wh/mol lithium

(considering 50% efficiency)

STABILIYY



1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
$q_{measured}/q_{theory}$
Extraction from brine (insertion)
Recovery of LiCl
0
5
10
15
20
25
30
35
40
45
50
55
cvcle number

Conclusions

$Li_{1-x}Mn_2O_4$ ($0 \leq x \leq 1$) Li^+ insertion electrode and Polypyrrole Cl^- selective electrode extract lithium chloride from natural brine:

a. Direct evidence of LiCl extraction
b. Fast
c. Environmentally friendly (water, waste, chemicals)
d. Low energy consumption (10 Wh/mol LiCl)
e. Highly selective (no co-insertion of Na^+)
f. Overall cell voltaje < 1V
g. Highly reproducible over > 200 + 200 extraction/recovery cycles.
h. 50% Faradaic efficiency due to carbon anodic oxidation.
i. XRD and CV evidence that Na^+ is no co-inserted with Li^+.
j. Surface adsorption/occlusion of NaCl requires careful rinsing.
k. Adsorption model applies to the Li^+ ion transfer at the $Li_{1-x}Mn_2O_4$ /brine interface.
l. Na^+ adsorption at $Li_{1-x}Mn_2O_4$ blocks sites for Li^+ adsorption

NEW LITHIUM RESEARCH CENTER IN JUJUY, ARGENTINA

Province of Jujuy, Argentina
CONICET
University of Jujuy

THANKS

https://www.sciencecanchangetheworld.org/