Almacenamiento de Energía: Baterías de Litio

"ENERGÍA SUSTENTABLE Y TRANSPORTE"

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INQUIMAE. DQIAyQF

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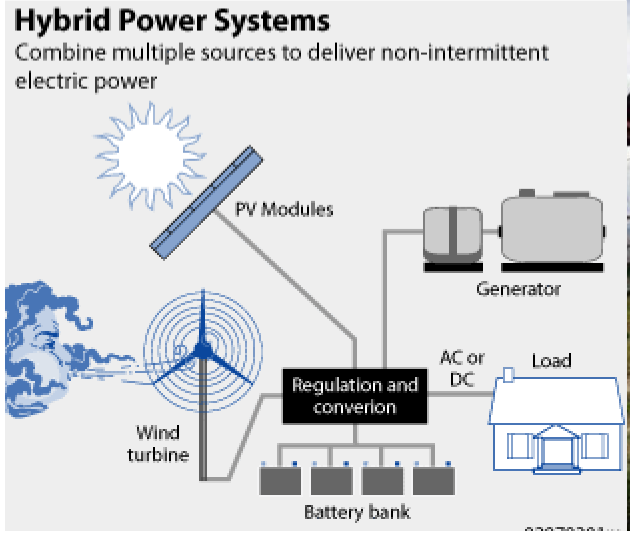
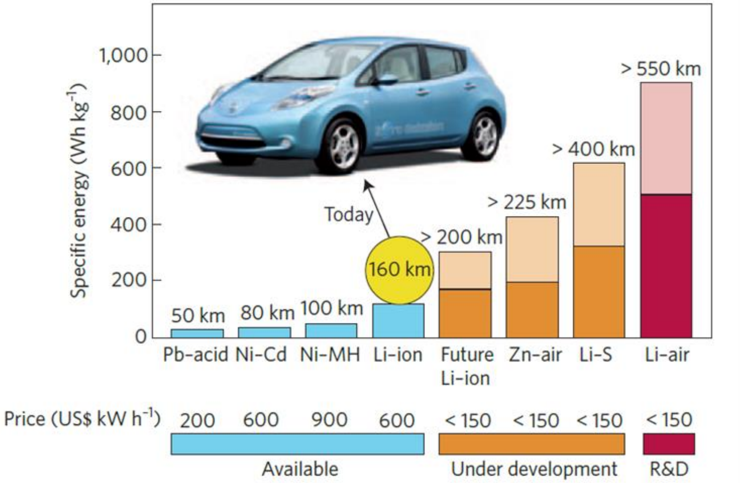


Remote Electrification (7.5 GWh market in South America)

Portable Electronics

Why is Lithium strategic for Energy Storage?

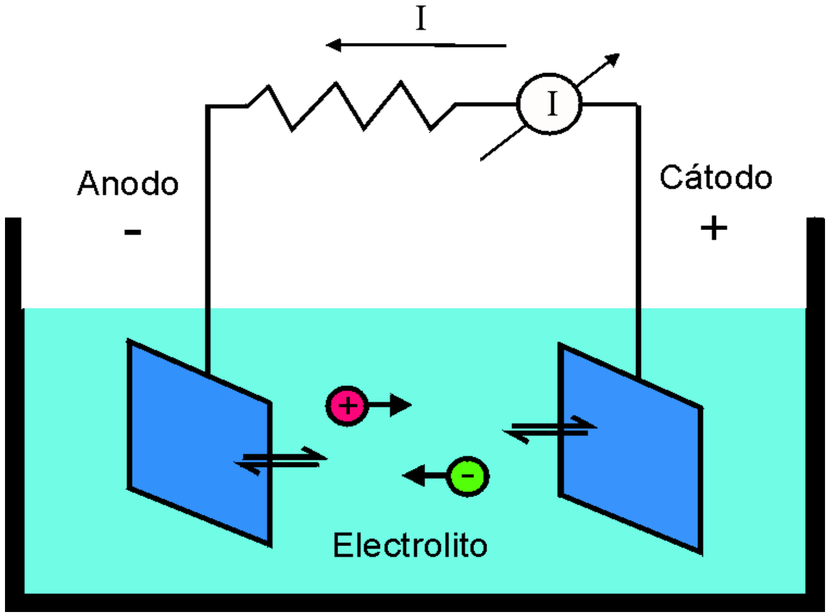


Electric Vehicles

¿ Dónde esta la química en mi celular?

Las baterías de ion litio desarrolladas por Sony en 1991 se utilizan ampliamente en dispositivos electrónicos portátiles como celulares, tabletas, laptops, herramientas, etc. Su funcionamiento se basa en la inserción de iones litio en la red cristalina de óxidos en el cátodo o carbono en el ánodo.

$$xLi^{+} + xe^{-} + 6C \rightleftarrows Li_xC_6$$

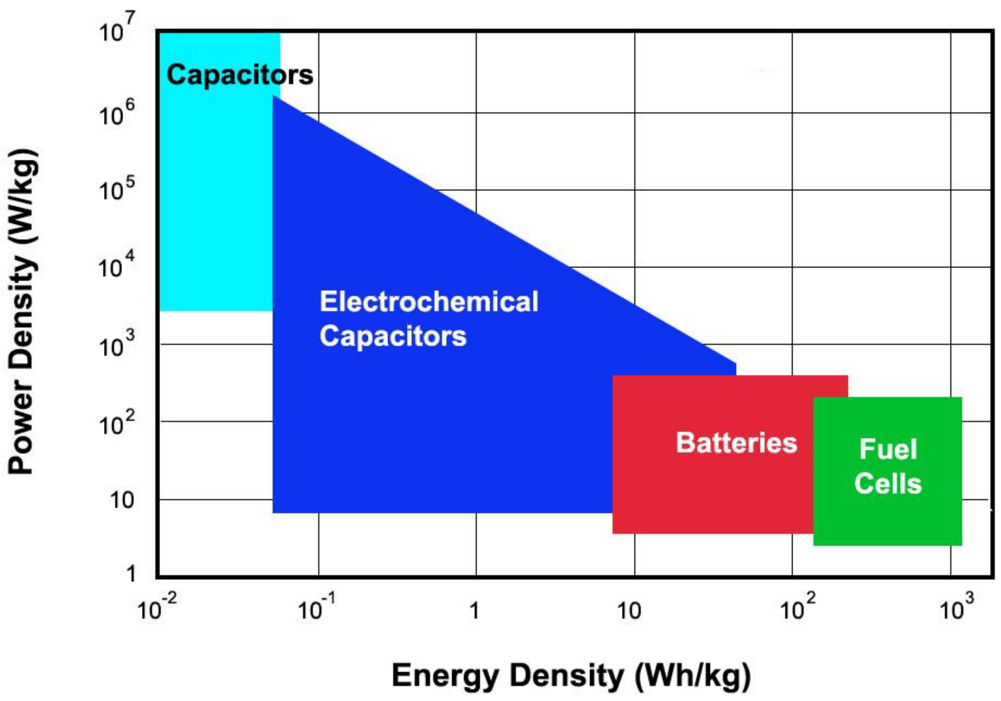


$$LiCo^{III}O_2 \rightleftarrows Li_{1-x}Co^{IV}_{x}Co^{III}_{1-x}O_2 + xLi^{+} + xe^{-}$$

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)

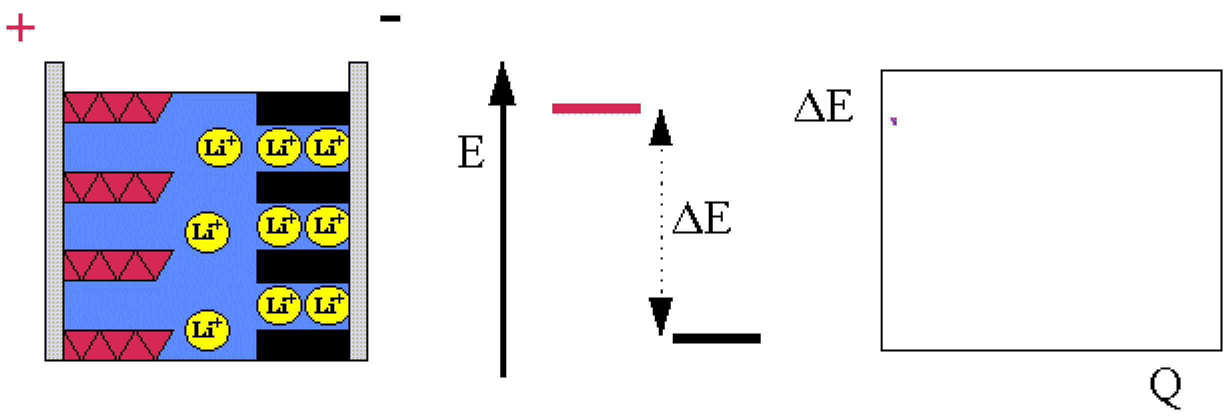


Batterias de ion Li^+

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

EL OBJETIVO PARA AUTOS ELECTRICOS

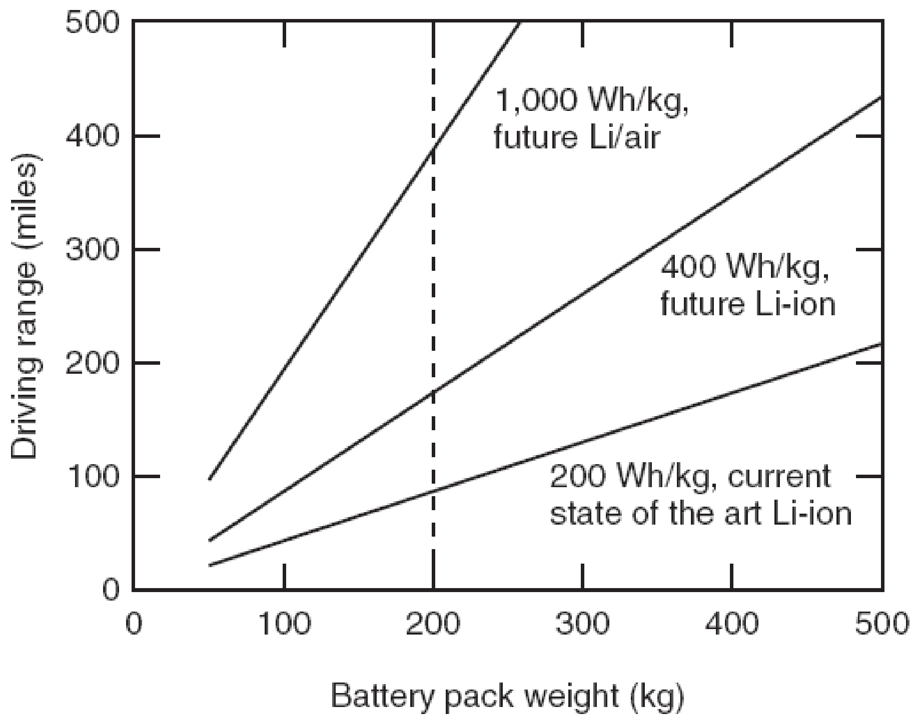
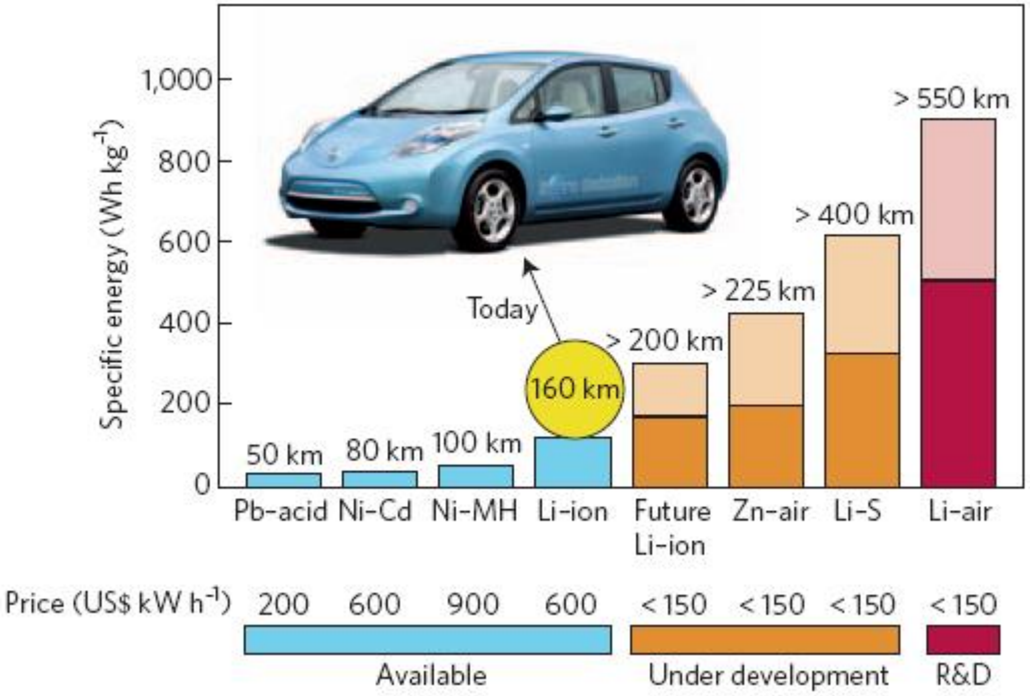


Figure 1. Driving range and battery weight for different cell-level specific energy values. It is assumed the battery cells weigh 70% of the battery pack, the Li/air cell has an 83% energy efficiency, the Li-on cells have a 93% energy efficiency, and 300 Wh/mile are required from the battery. The range is given at the beginning of a battery's life and assumes 100% of the capacity can be used; in practice not all the energy can be used, and the available energy falls with increasing battery age. The US Department of Energy has a goal for an EV battery of 200 kg.[176]

A Critical Review of Li/Air Batteries

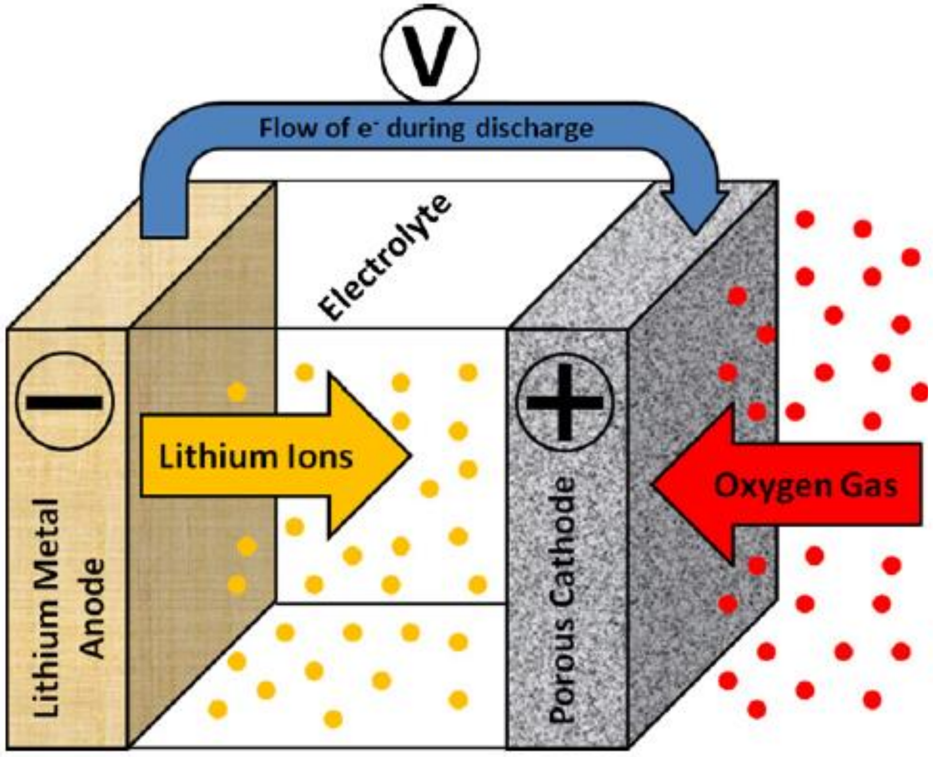
J. Christensen, P. Albertus, R.S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, A. Kojica

Journal of The Electrochemical Society, ***159 (2) R1-R30 (2012)***



Battery	Cell voltage (V)	Theoretical specific energy (Wh kg^{-1})	Theoretical energy density (Wh l^{-1})
Today's Li-ion $\frac{1}{2}C_6Li + Li_{0.5}CoO_2 \leftrightarrow 3C + LiCoO_2$	3.8	387	1,015
Zn-air $Zn + \frac{1}{2}O_2 \leftrightarrow ZnO$	1.65	1,086	6,091* (ZnO)
Li-S $2Li + S \leftrightarrow Li_2S$	2.2	2,567	2,199† ($Li + Li_2S$)
Li-O_2 (non-aqueous) $2Li + O_2 \leftrightarrow Li_2O_2$	3.0	3,505	3,436‡ ($Li + Li_2O_2$)
Li-O_2 (aqueous) $2Li + \frac{1}{2}O_2 + H_2O \leftrightarrow 2LiOH$§	3.2	3,582	2,234‖ ($Li + H_2O + LiOH$)

Baterías Recargables de Li Aire



$$2Li + O_2 \rightarrow Li_2O_2$$

$$2Li + (1/2)O_2 \rightarrow Li_2O$$

Anodo

$$Li \leftrightarrow Li^+ + e^-$$

Catodo

$$2(Li^+ + e^-) + O_2 \leftrightarrow Li_2O_2(\text{solid})$$

$$4(Li^+ + e^-) + O_2 \rightarrow 2Li_2O \qquad U_0 = 2.91\ V$$

$$Li_2O_2 + 2(Li^+ + e^-) \rightarrow 2Li_2O \qquad U_0 = 2.72\ V$$

DESAFIOS TECNOLOGICOS

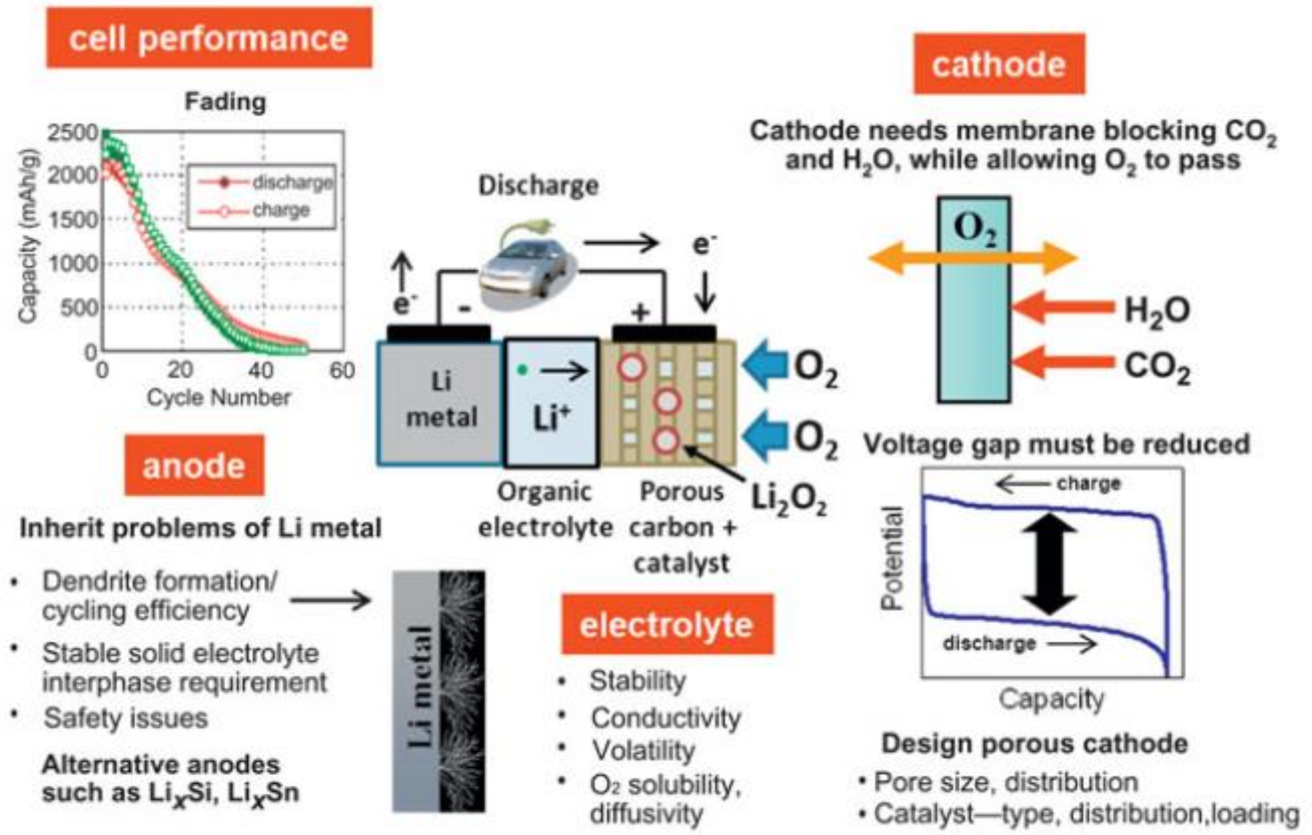


Figure 3. Challenges facing the non-aqueous Li-air battery.

¿COMO ES UNA BATERIA DE ION LITIO POR DENTRO?

cilindrica

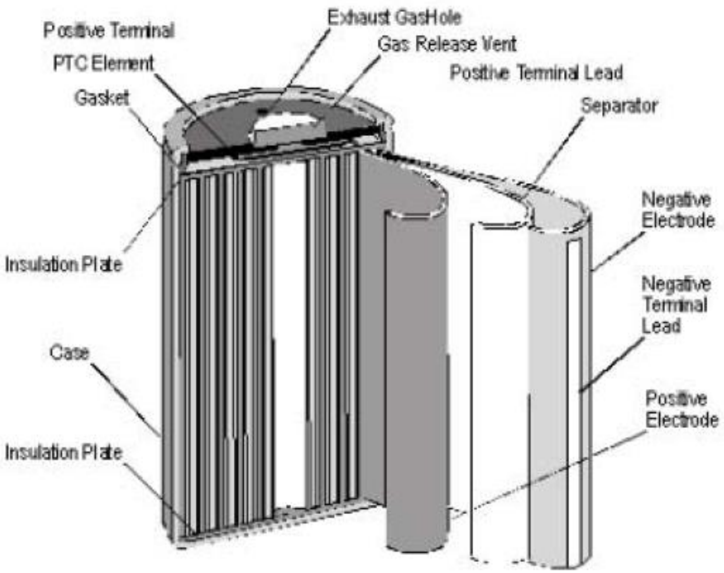
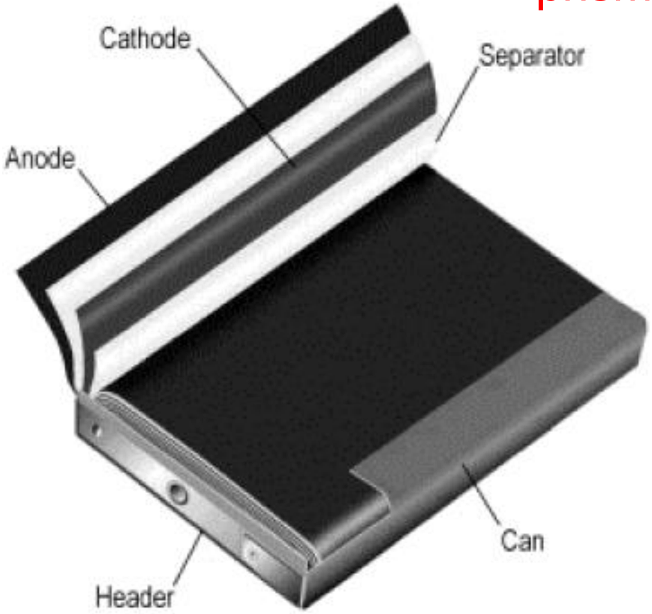


Figure 3-1: **Cross-section of a classic NiCd cell.**

prismatica



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

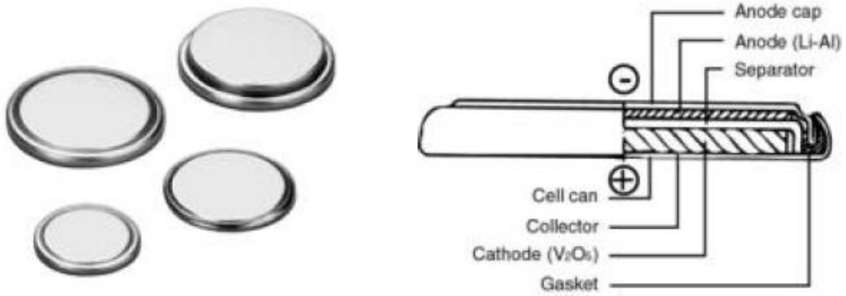
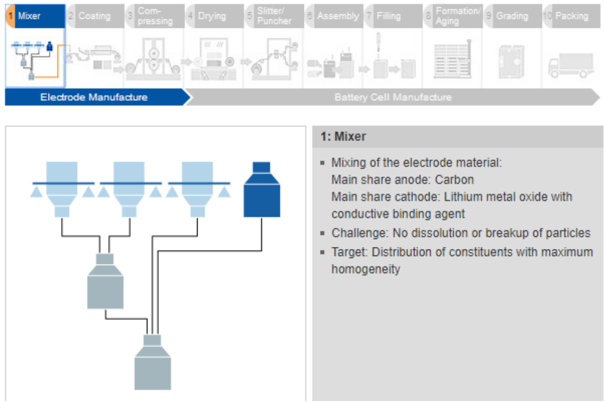


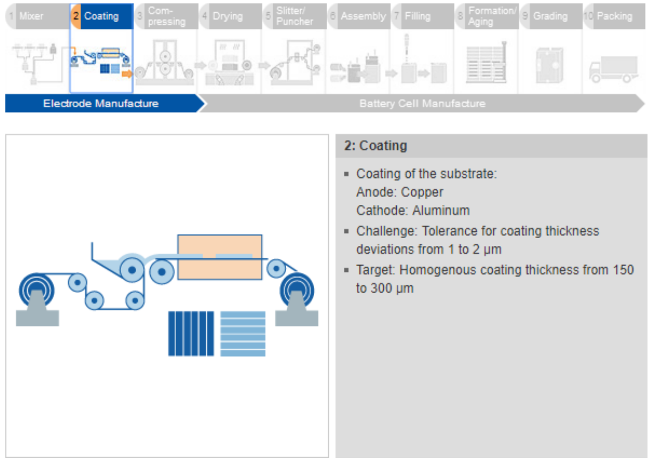
Figure 3-2: **The button cell.**

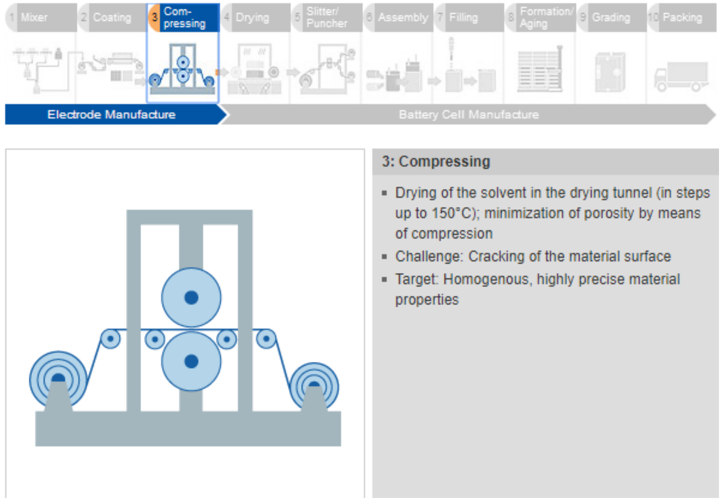
boton

Swiss roll

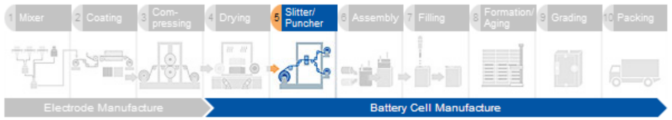
Fabricación de Baterías de Ión Litio





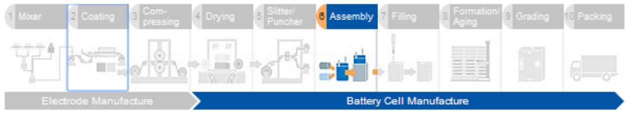


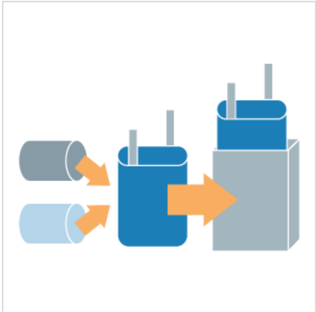
Planta piloto de baterías de ion litio en Potosí, Bolivia.



5: Slitter/Puncher

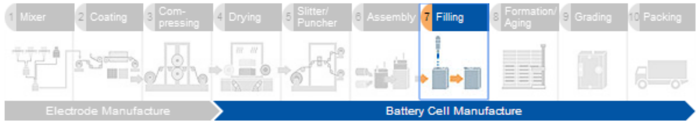
- Film cutting by means of highly precise cutting / punching / laser tools
- Challenge: Avoidance of burr formation, fraying of edges or material particles on the surface

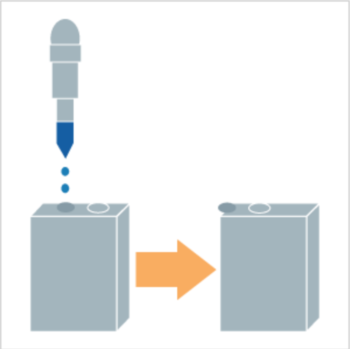




6: Assembly

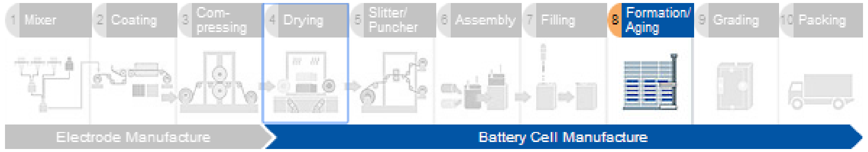
- Stacking of cells; integration in housing, contacting of electrodes; partial sealing of housing
- Challenge: Positioning accuracy of ~ 0.1 mm
- Target: Stacking process with approx. 80 layers per cell at maximum speed

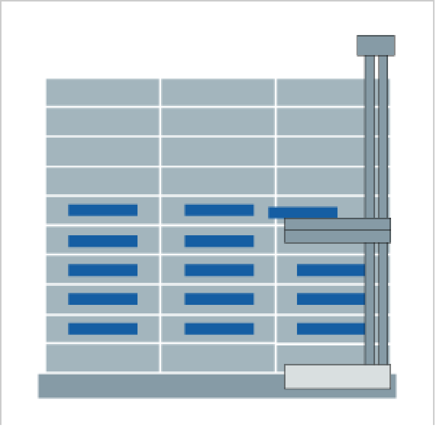




7: Filling

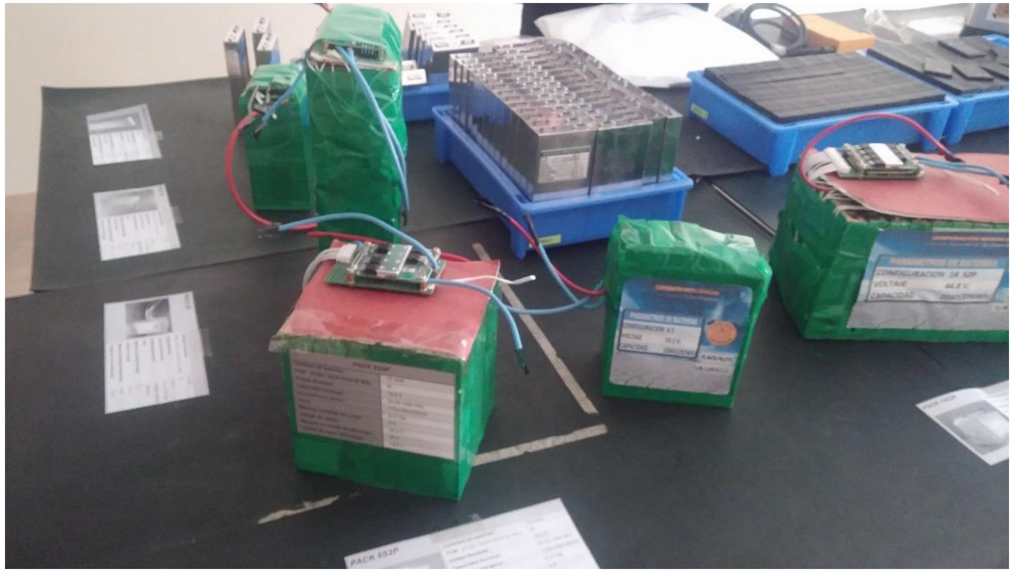
- Evacuation, electrolyte filling, sealing and cleaning of the cell in the dry room
- Challenge: Toxic reaction with air humidity! Varying absorptivity, blistering
- Target: Rapid and homogeneous filling of the cell





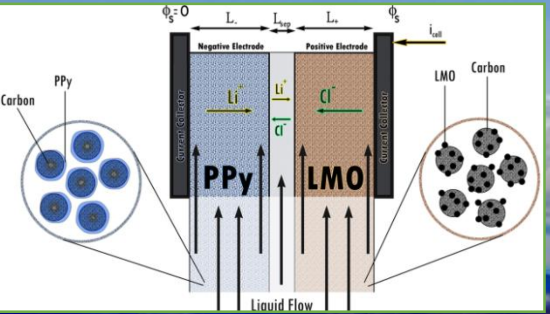
8: Formation/ageing

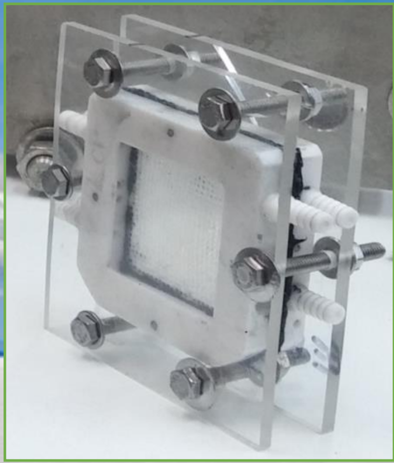
- Activation by means of charging / discharging routines with gradually increasing voltage storage for 2 to 4 weeks
- Challenge: High time and cost expenditures, increased risk of fire
- Target: Assurance of operability; preparation for categorization



Lithium extraction process for renewable energy storage

A SUSTAINABLE SOLUTION FROM INQUIMAE





Lithium battery storage enables renewable energy

- Mobile Electronics
- Remote Electrification
- Electric Vehicle

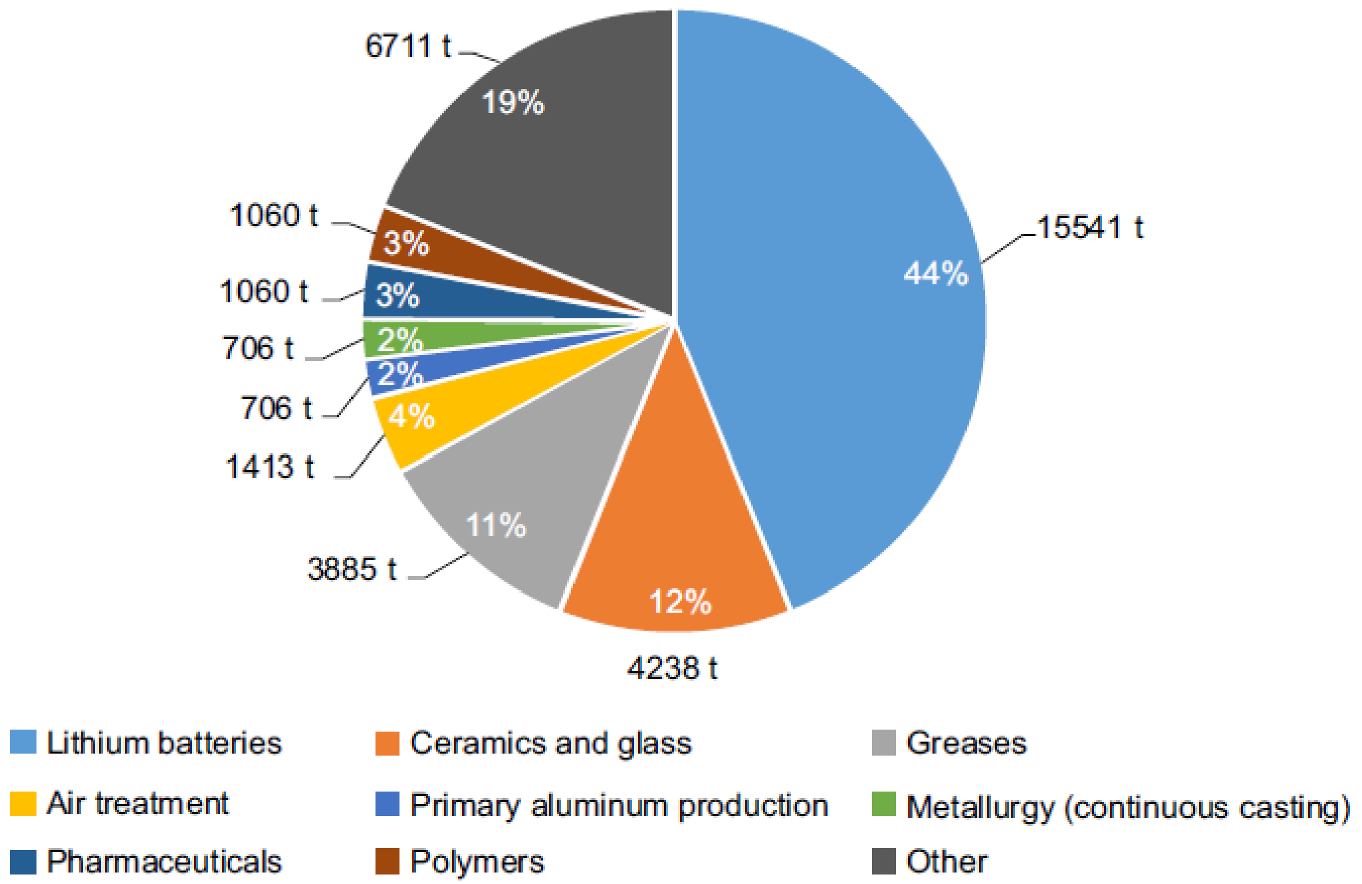
- Clean
- Fast
- Li ion Selective
- Modular
- Social Responsability

25,000 cars in the quarter january-march 2017

Lithium Batteries for Electric Car	Lithium Battery for a cell phone
450 kg battery 400 V cc. 60/75/90 kW (156 Wh/kg)	4.9 Wh
7104 cellx x 2,4 V = 17.050 Ah	1.32 mAh
4,453 g Li	0.344 g

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

USES OF LITHIUM



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

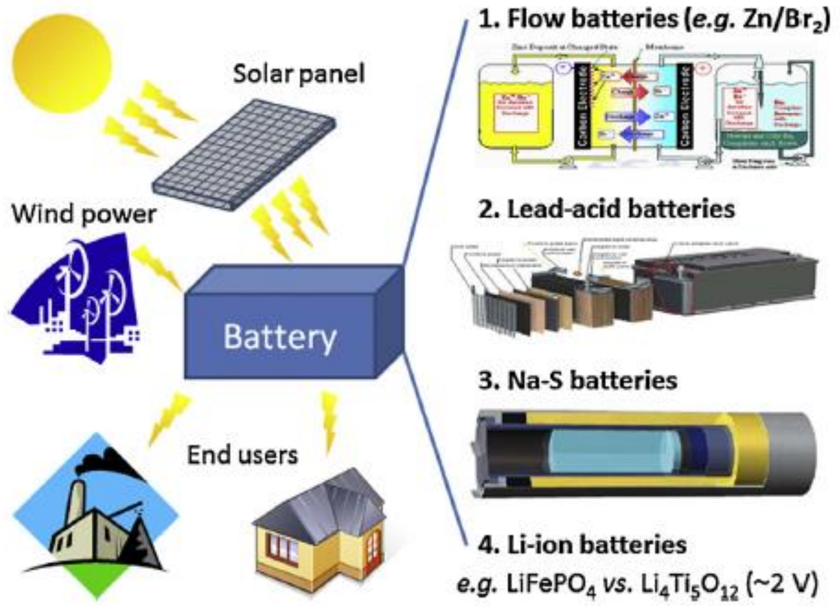
LITHUM BATTERY FOR SUSTAINABLE ENERGY STORAGE

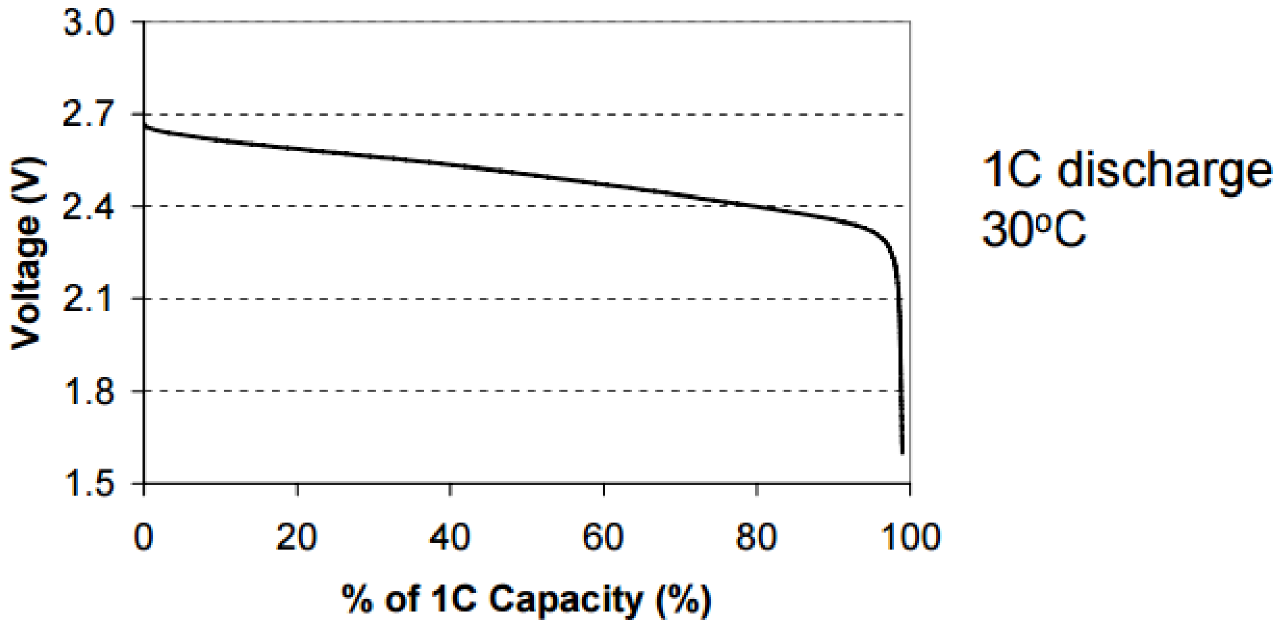
Positive Active Material (LMO):

$$LiMn_2O_4 \rightarrow Li_{1-x}Mn_2O_4 + xLi^+ + xe$$

Negative Active Material (LTO):

$$Li_4Ti_5O_{12} + \ xLi^+ + xe \rightarrow Li_{4-x}Ti_5O_{12}$$





E_{cell} = 2.5 V

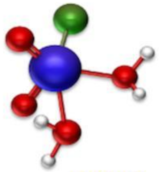
LTO/LMO battery
Much higher available energy and voltage than Ni-MHO

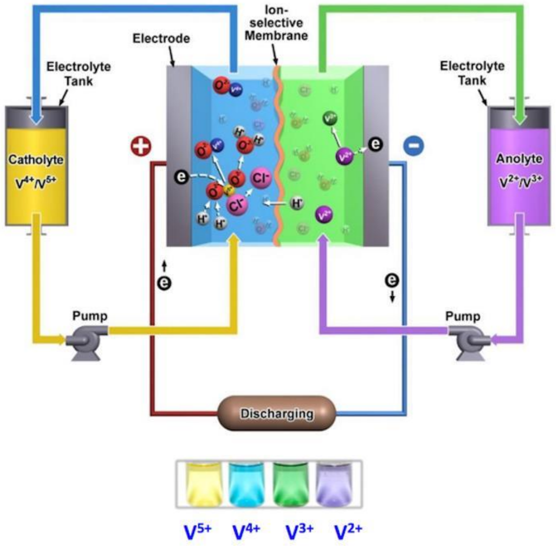
- **Advantages LTO**
- High Power, less impedance than graphite
- Outstanding Safety
- No SEI layer. No lithium dendrites
- Remote risk of thermal runaway
- Stable active materials
- Long Life
- Zero strain material (LTO ~ 0.2 % volume change) vs. Graphite ~ 9% volume change)
- Low temperature performance
- More electrolyte choices
- Disadvantages
- Lower Energy Density
- Low Cell Voltage. (1.5V on negative)

- **<u>Advantages </u>LMO**
- High Voltage
- High voltage profile to couple with lithium titanate
- Low Cost Low LMO (3/4 of $LiFePO_4$, 1/2 of LiNiCo Oxide, 1/3 of $LiCoO_2$.
- Power Capability
- Outstanding Safety
- O_2 under high temperature.

BATERIAS EN FLUJO

International Flow Battery Forum in Karlsruhe
Fraunhofer Institute for Chemical Technology ICT



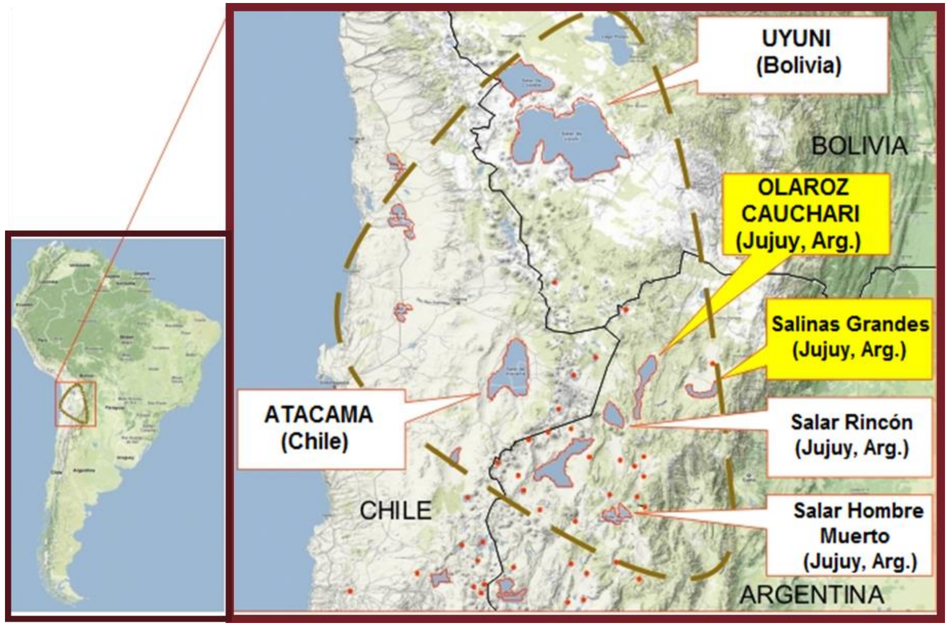


20 MWh all vanadium redox flow cell for stationary applications for 2 MW wind turbine
75% efficiency in current technical solutions
10,000 additional cycles
Cost 0.05 $us/kWh
UniEnergy Technologies (UET) of Seattle, 2MW/8MWh
Dalian China planned by Rongke, 200MW/800MWh.

Table I. Characteristics of Some Flow Battery Systems.

System	Reactions	E_{cell}^{o}	Electrolyte
Redox			Anode/Cathode
All Vanadium [3]	Anode: $V^{2+} \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} V^{3+} + e^-$ Cathode: $VO_2^+ + e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} VO^{2+}$	1.4 V	H_2SO_4/H_2SO_4
Vanadium-Polyhalide [5]	Anode: $V^{2+} \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} V^{3+} + e^-$ Cathode: $\frac{1}{2} Br_2 + e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} Br^-$	1.3 V	VCl_3-HCl/NaBr-HCl
Bromine-Polysulfide [6]	Anode: $2\,S_2^{2-} \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} S_4^{2-} + 2e^-$ Cathode: $Br_2 + 2e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} 2\,Br^-$	1.5 V	$NaS_2/NaBr$
Iron-Chromium [7]	Anode: $Fe^{2+} \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} Fe^{3+} + e^-$ Cathode: $Cr^{3+} + e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} Cr^{2+}$	1.2 V	HCl/HCl
H_2-Br_2 [8]	Anode: $H_2 \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} 2H^+ + 2e^-$ Cathode: $Br_2 + 2e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} 2Br^-$	1.1 V	PEM*-HBr
Hybrid			
Zinc-Bromine	Anode: $Zn \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} Zn^{2+} + 2e^-$ Cathode: $Br_2 + 2e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} 2\,Br^-$	1.8 V	$ZnBr_2/ZnBr_2$
Zinc-Cerium [9]	Anode: $Zn \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} Zn^{2+} + 2e^-$ Cathode: $2Ce^{4+} + 2e^- \xleftarrow{\text{charge}}\xrightarrow{\text{discharge}} 2Ce^{3+}$	2.4 V	CH_3SO_3H (both sides)

Where?



In 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)

Why?

30 million people off grid, i.e., a 7.5 GWh market for remote electrification
Lithium batteries for off peak energy storage with > 15 year life time
Lithium ion batteries are well suited for this.


Salar Hombre Muerto. FMC
Catamarca, Argentina

WORLD LITHIUM PRODUCTION

Country/year	2010	2011	2012	2013	2014	2015
Australia	49.205	66.530	68.127	67.594	70.708	71.320 (40%)
Chile	55.938	68.659	70.256	59.611	61.208	67.594 (38%)
China	21.023	22.035	23-951	25.015	12.242	11.709 (6,6%)
Argentina	15.701	15.701	14.370	13.306	17.032	20.225 (11,4%)

World extractable resources 10 million tons (2010 Stanford University)

10^3 x Ton	2012	2013	2014	2015	2016	2017	2018
Supply	171	166	184	189	201	205	207
Demand	164	171	180	188	204	229	258
	+7	-5	+4	+1	-3	-24	-51

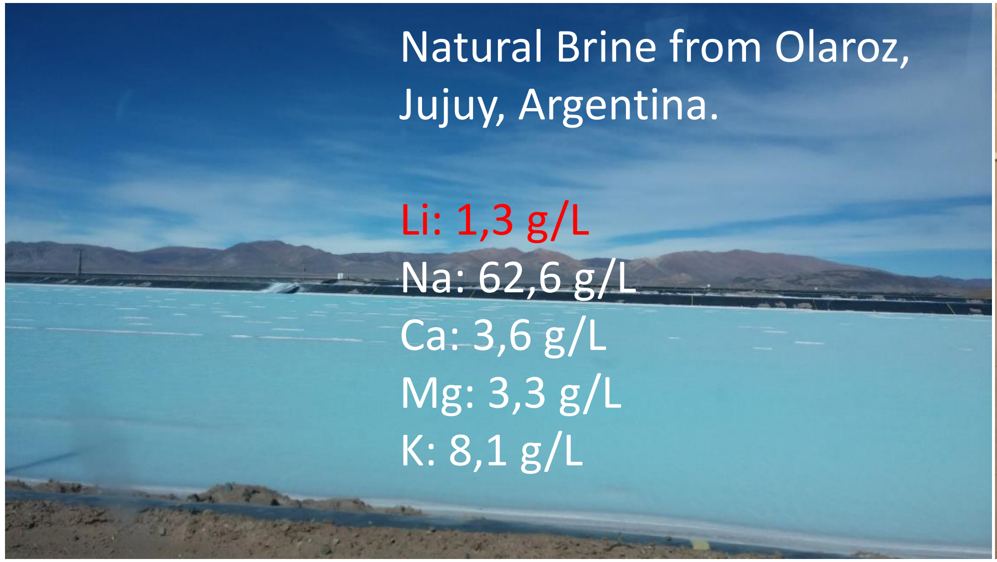
Roskill Company Report 2016

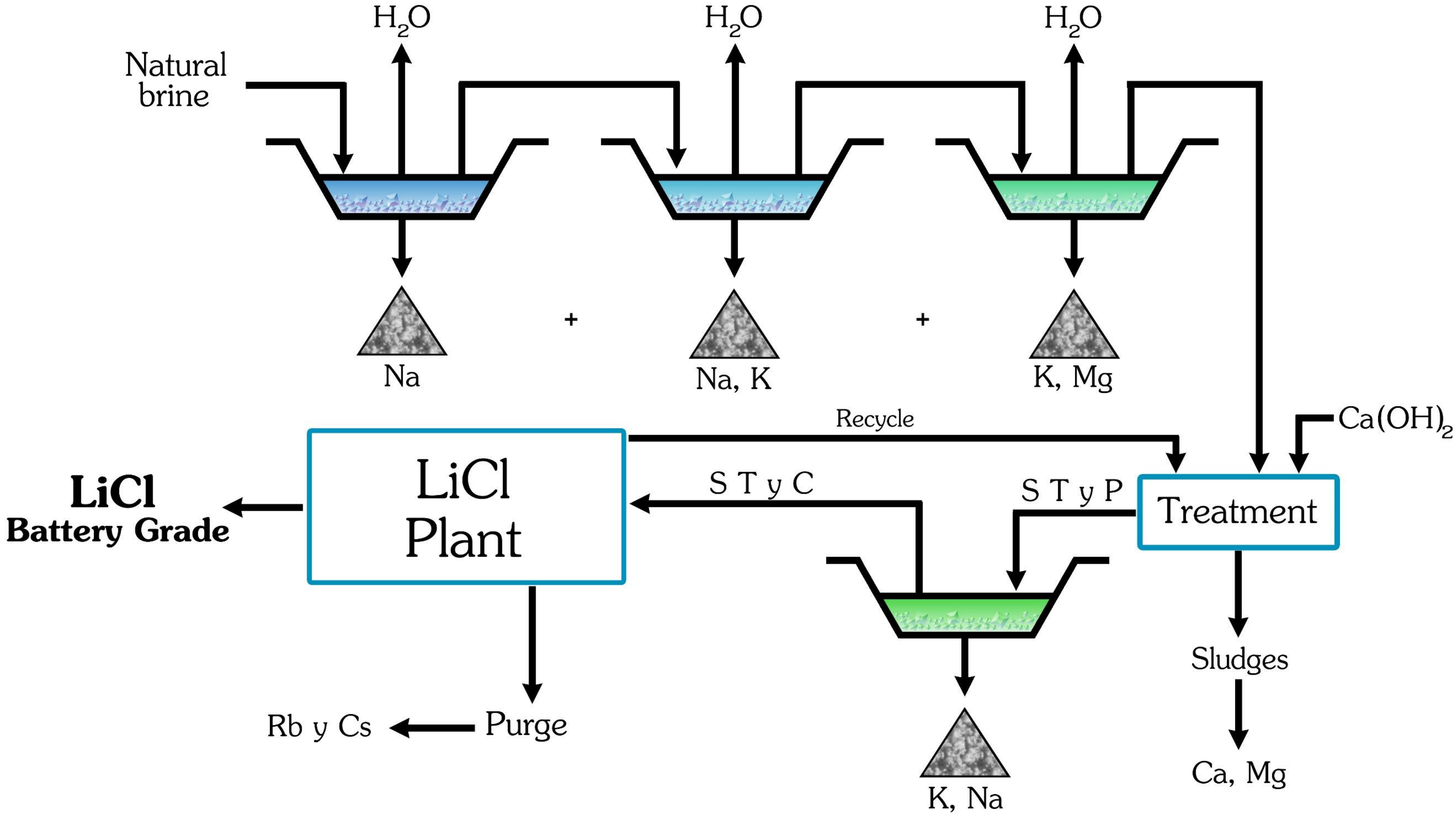
International Price rose fom 6.000 to 15-20.000 per ton of lithium carbonate

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)





Natural brine
H2O
H2O
H2O
Na
+
Na, K
+
K, Mg
Recycle
Ca(OH)2
LiCl Plant
S T y C
S T y P
Treatment
LiCl
Battery Grade
Sludges
Purge
Rb y Cs
K, Na
Ca, Mg

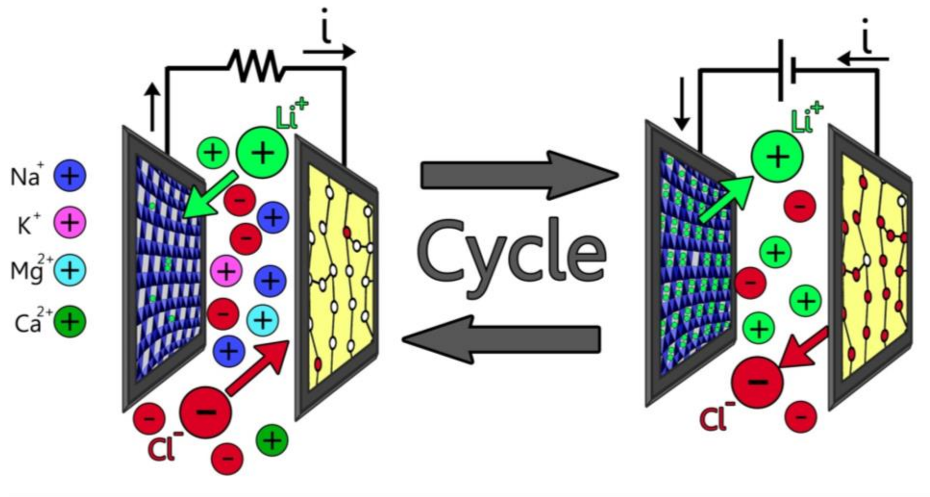
CHEMICAL COMPOSITION OF BRINES FROM SALT FLATS

	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

OUR SOLUTION

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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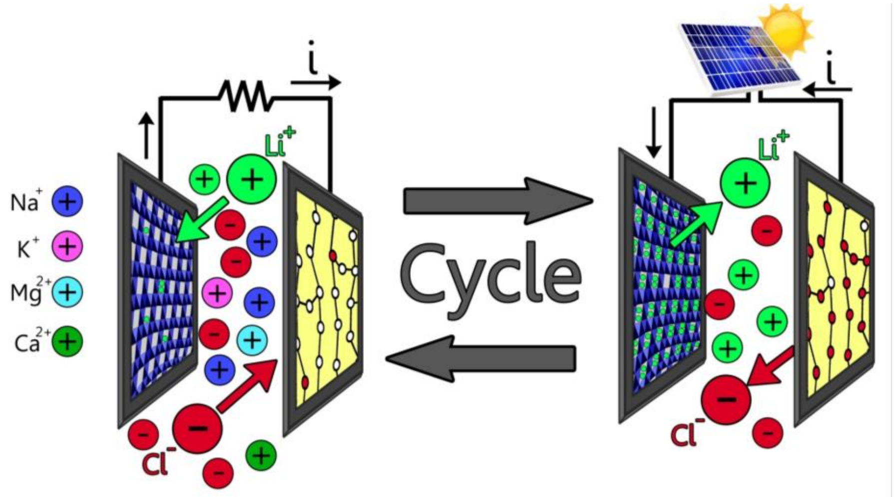

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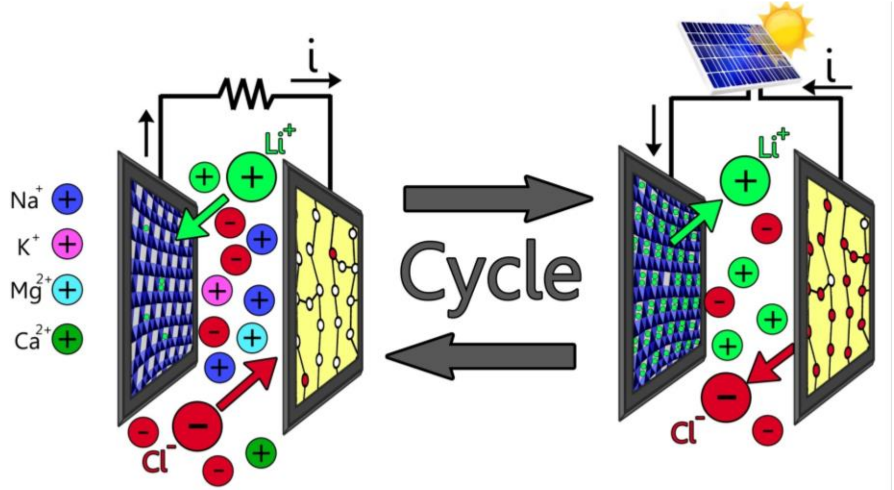
Two step electrochemical process

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

What is unique?

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

Premium Solar energy

↓

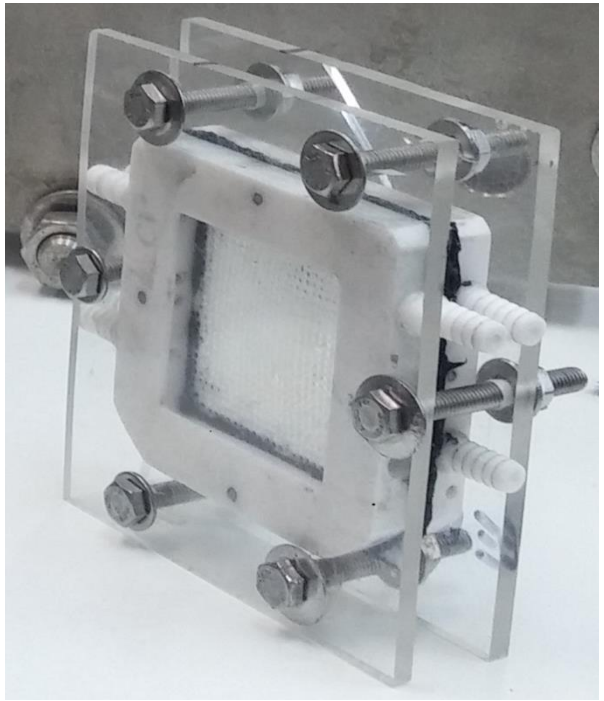
Extract lithium chloride

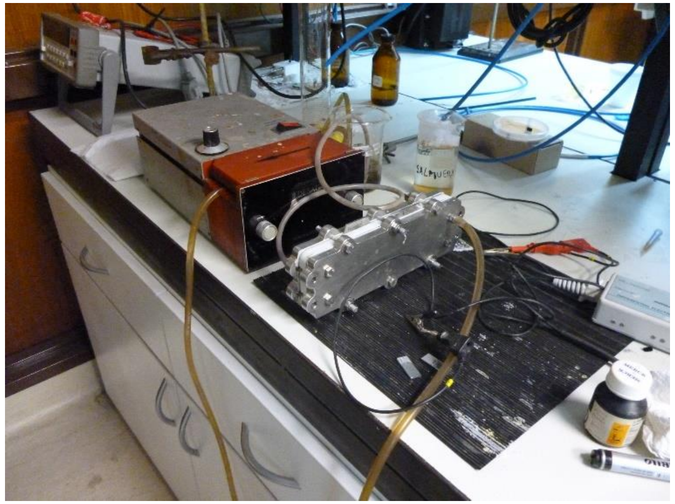
↓

Lithium batteries

↓

Intermittent renewable energy storage



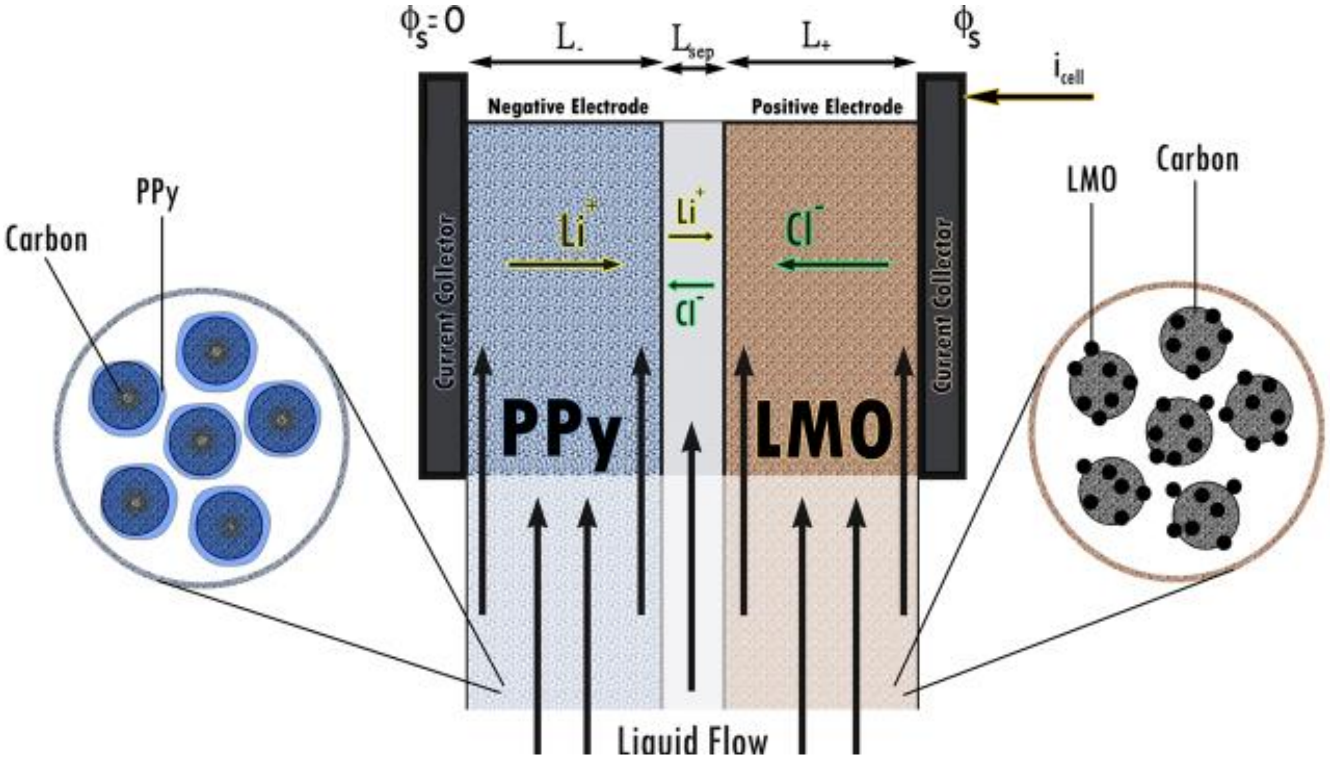


ELECTROCHEMICAL REACTOR

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

POLYPYRROLE (PPy) CHLORIDE SELECTIVE SUPERCAPACITOR POROUS ELECTRODE

ELECTROLYTE SEPARATOR

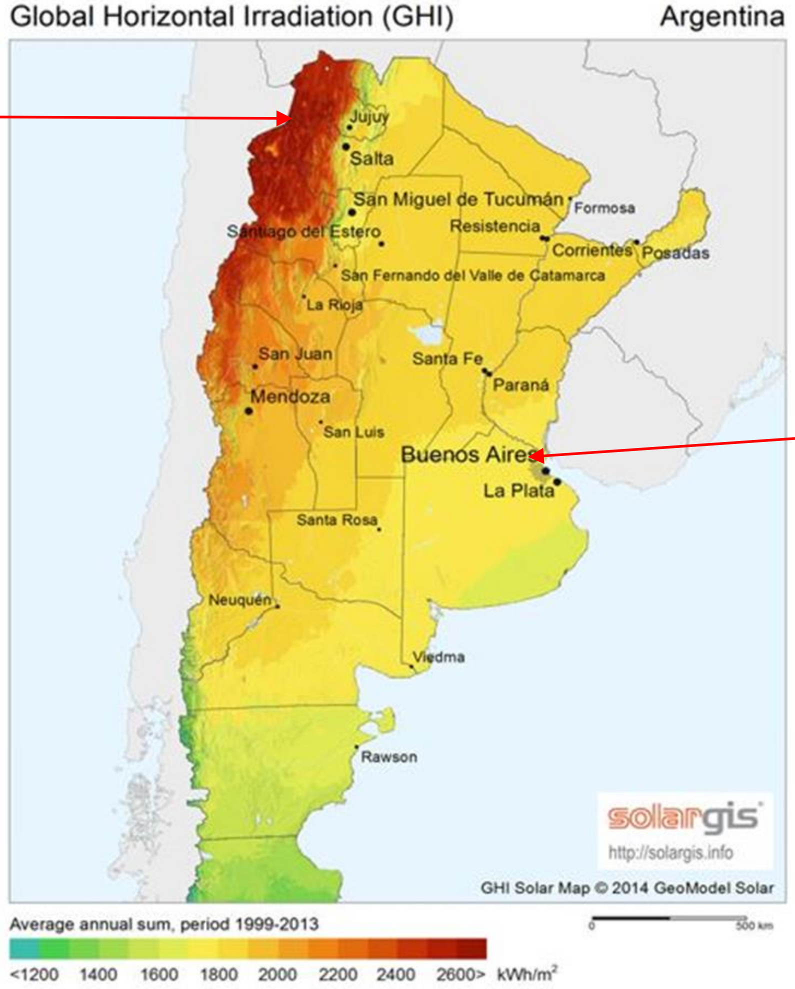


A REGION WITH PREMIUM SOLAR ENERGY (> 2600 kWh/m²)

Li rich brines in
Salt Flats
at 4000 meters

Solar Radiation
> 2600 kWh/m²

New CONICET
Center for
Lithium Research



University of Buenos
Aires
CONICET
Science and Technology

ENERGY COST

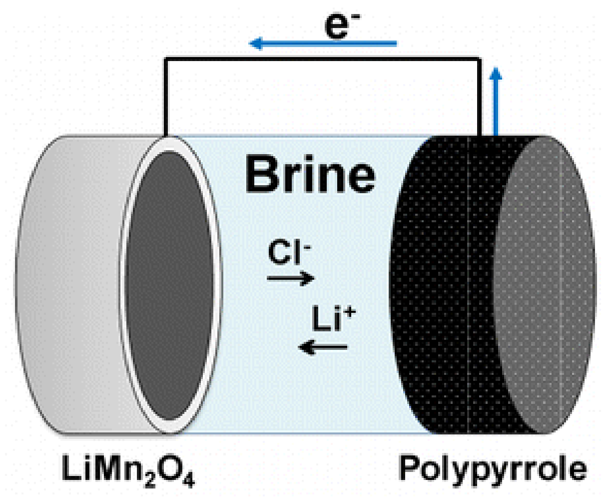
Low energy consumption 0.7 kWh/Kg of Li (power an iphone once a day for a year)

At 10 cents of dollar per kWh, it will cost 70 $ to produce a ton of lithium salt at a world market value of 10,000-20,000 $ per ton.

CAPITAL INVESTMENT 10 $us/ton!!

The electricity needed for the novel extraction process from solar panels

- 700 Kwh/metric ton Li
- Solar Panels at 2000 $us/ kW
- 50 kW $\rightarrow$700 kWh/day$\rightarrow$1 Ton Li/day
- Investment 100.000 $us $\rightarrow$800 m^2 $\rightarrow$ 30 years $\rightarrow$11.000 Ton

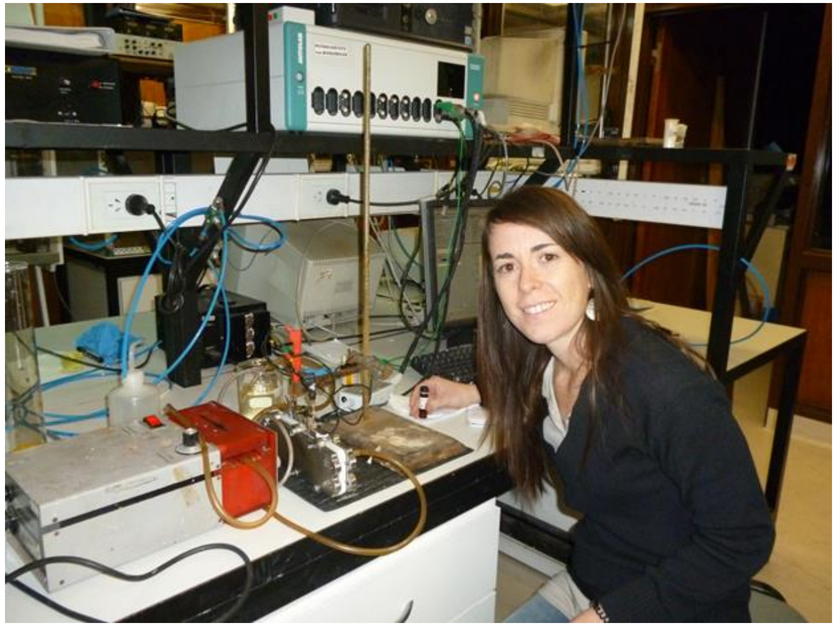


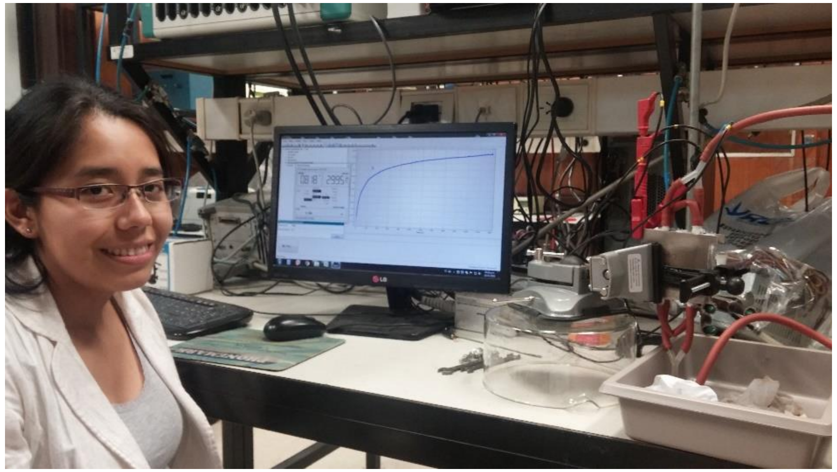
Who will benefit?

Local communities
local governments
companies extracting lithium
manufacturing and using lithium batteries

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

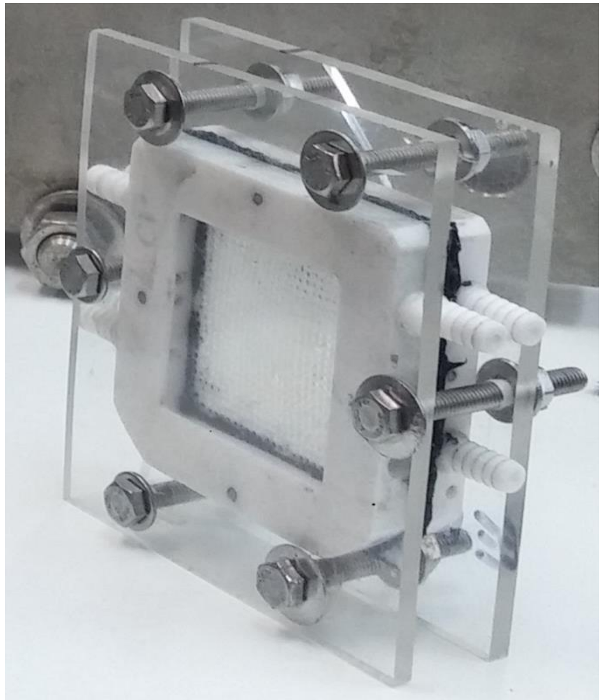
Unit Process

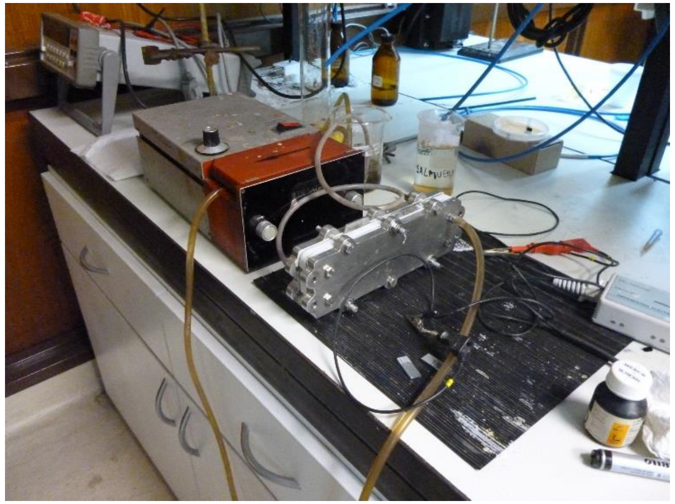
WHERE WE WANT TO GO?

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

ELECTROCHEMICAL REACTOR





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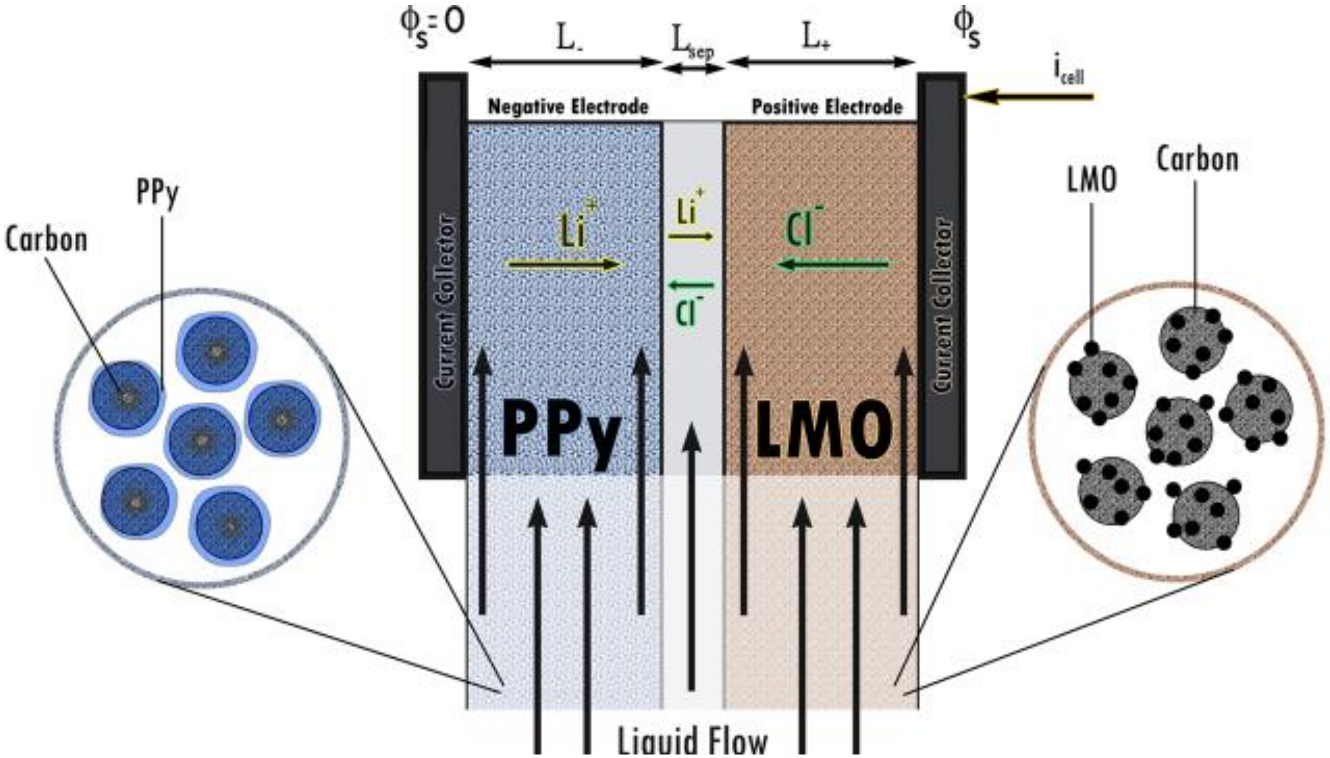


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MUCHAS GRACIAS