Chemistry of Materials, Energy and Environment for a clean and sustainable world

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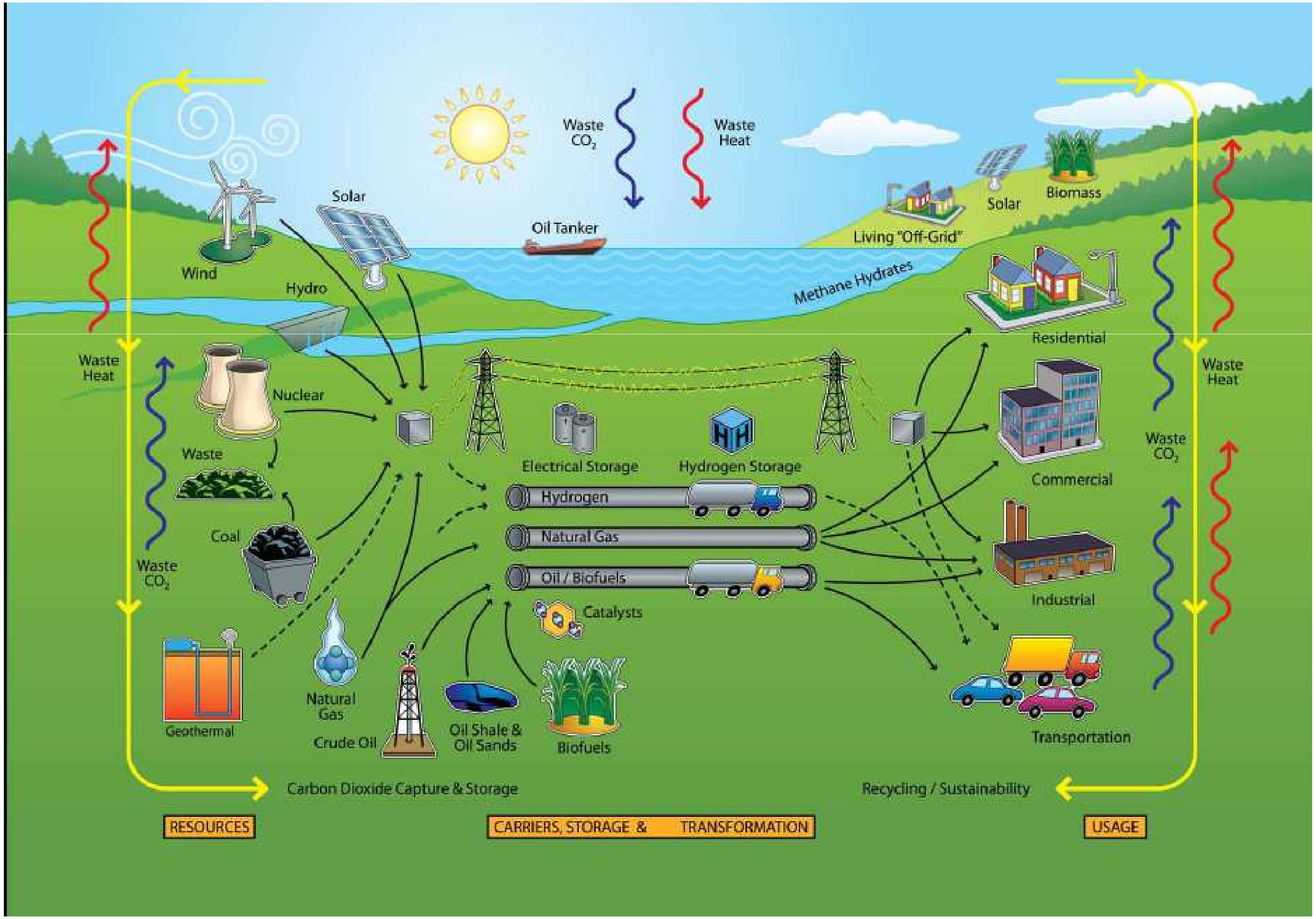
INSTITUTE OF CHEMISTRY OF MATERIALS, ENVIRONMENT AND ENERGY

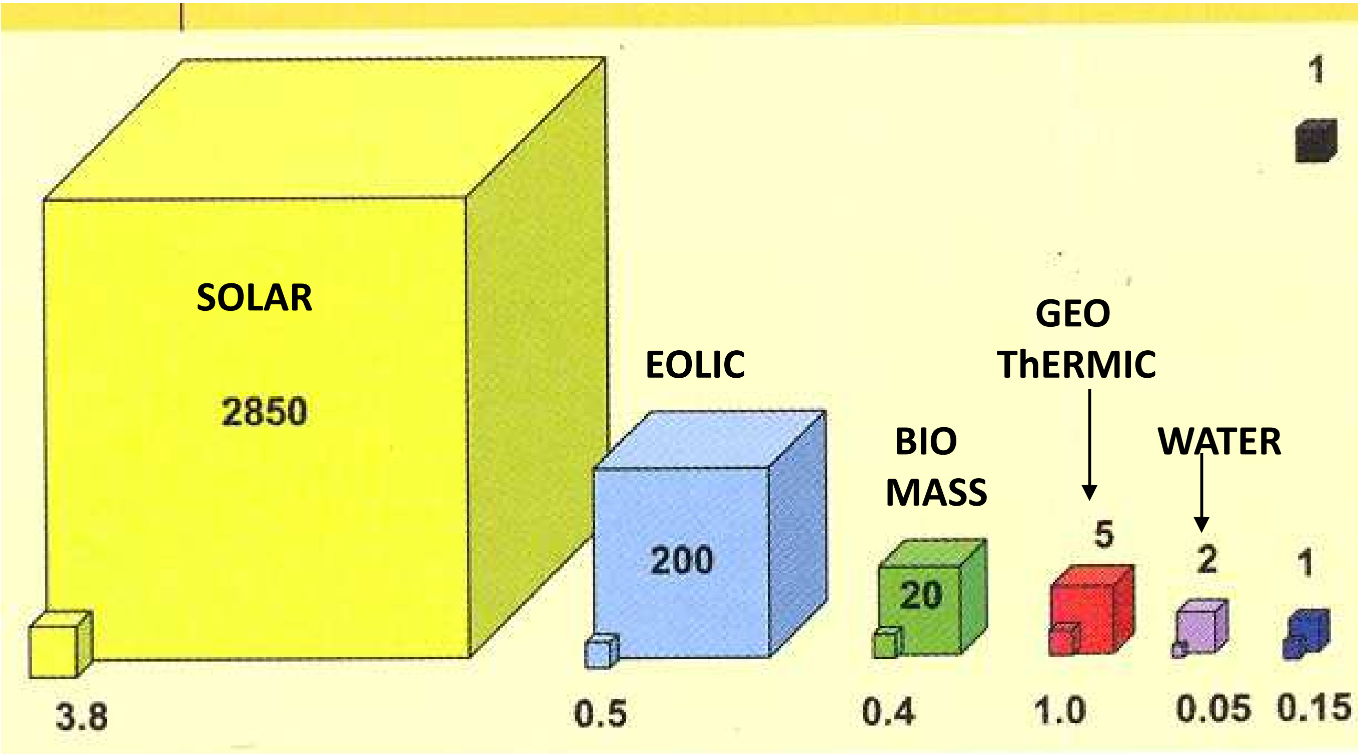
INQUIMAE

ORGANIZATION

Chemistry in the cycle of production, transport and consumtion of energy



Renewable resources in relation to world energy consumption

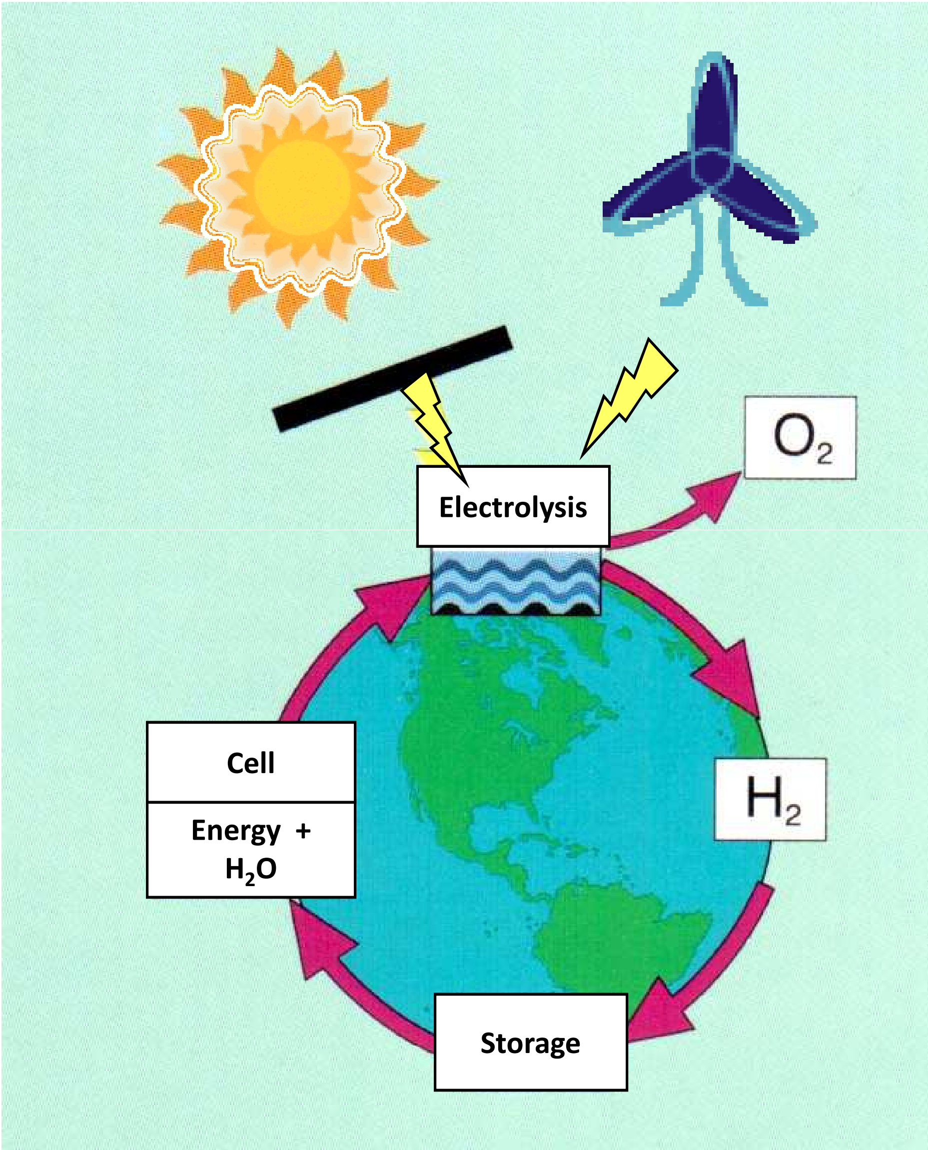


Present energy consumption

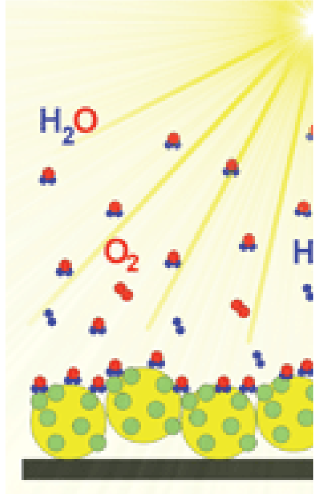
Technically and enconomically exploitable

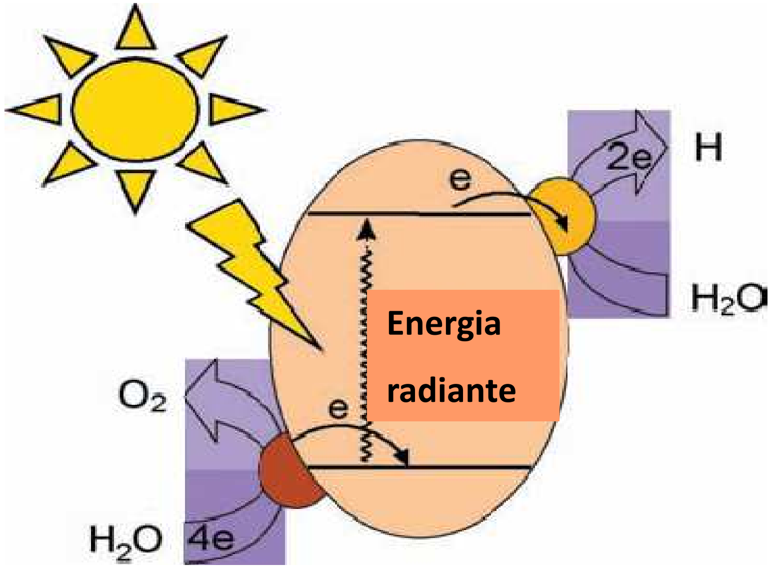
R. Wengenmayr, T. Bührke, Renewable Energy, Wiley-VCH (2006)

Renewable sources> Clean alternative

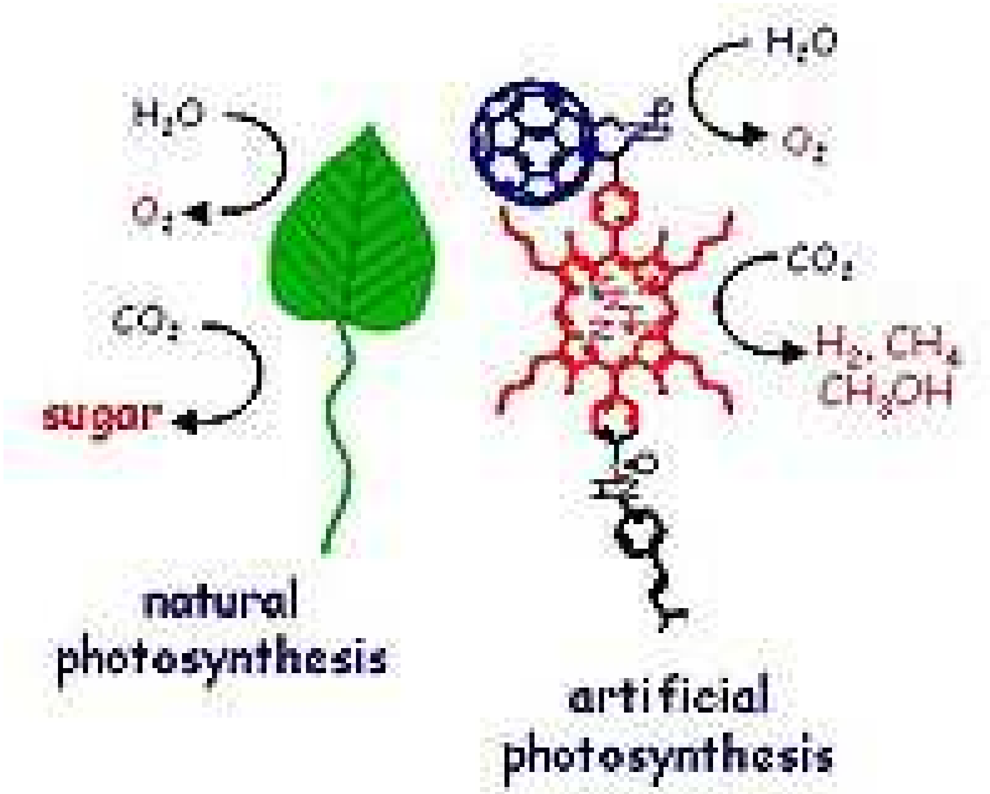


Hydrogen for water splitting



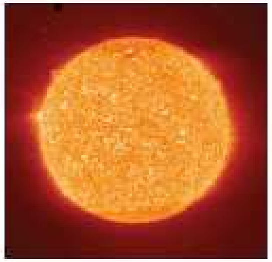


Challenges: wavelength for the process out of UV range (~2% solar radiation) and move into visible range



Biomimetics, copy Nature?

Energy storage is critical for the use of renewable energies for electronic devices and electric vehicles (EV y HEV)



US in 1900

1500 electric cars compared with 1000 ICE cars

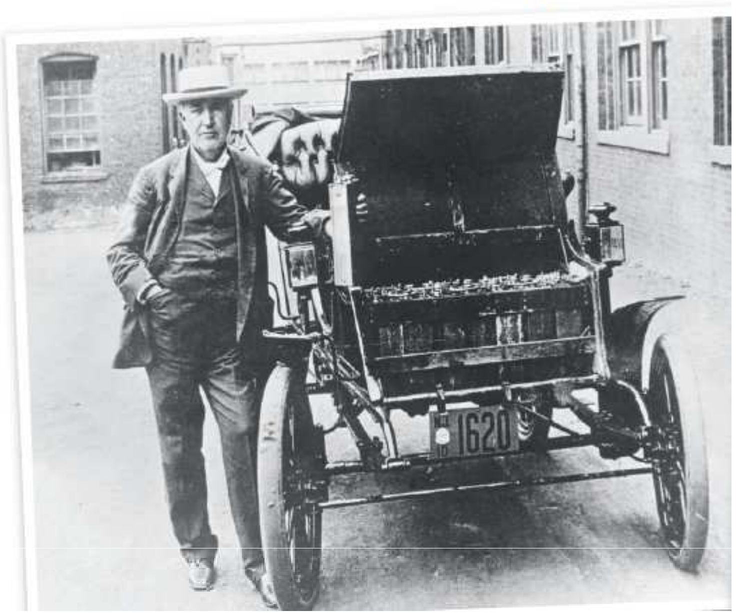
Li-ion batteries:

Cell phone 1 Ah
1 A.h 3,6 V

Laptop
4-5 A.h 11 V

Electric Vehicle
100 A.h

Chemistry of Materials for Energy Storage with low Environment Impact



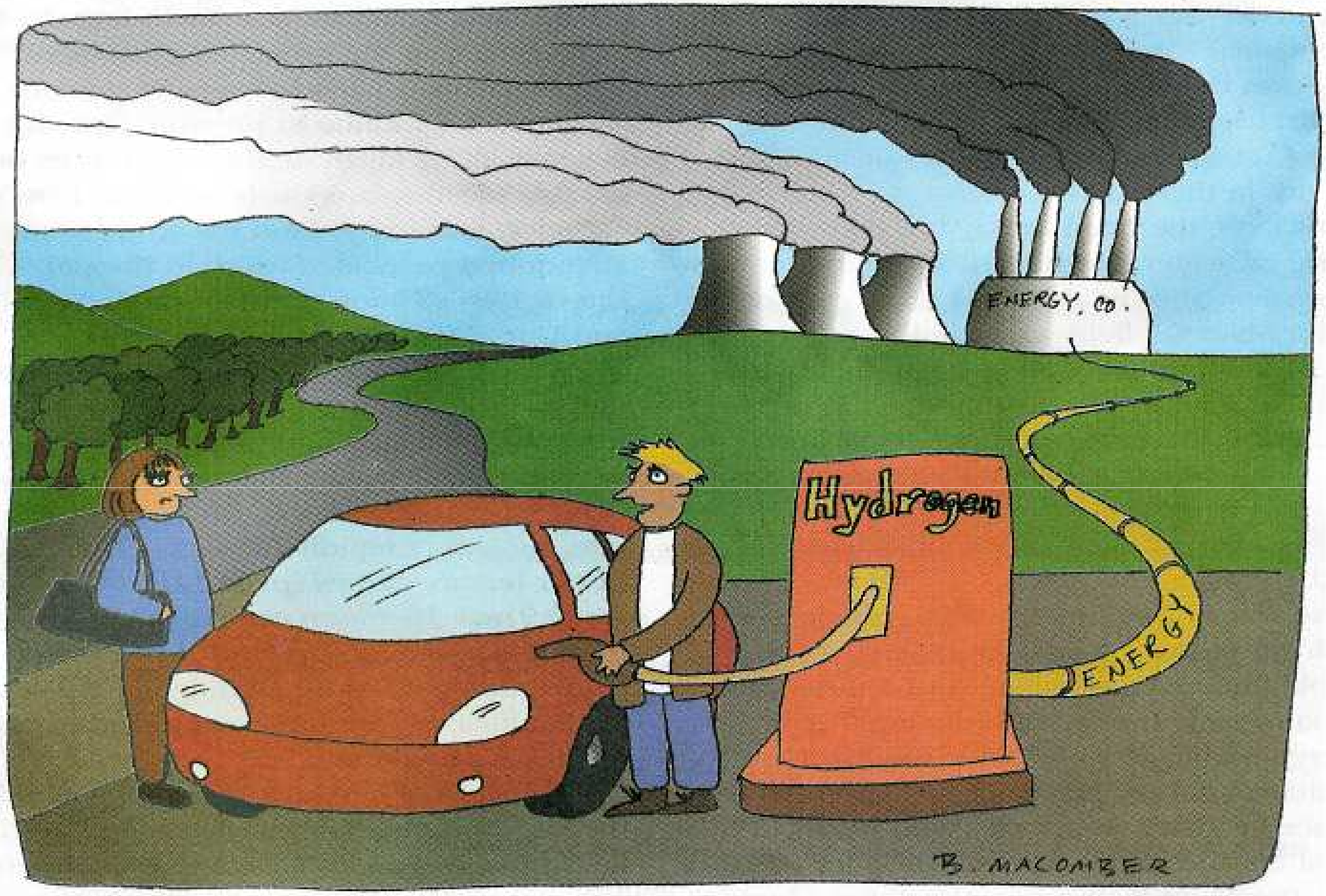
a) Hybrid Electric Vehicles (HEV)
b) Plugged Electric Vehicles
c) Electric Vehicles (EV)

14 Terawatts world energy consumption

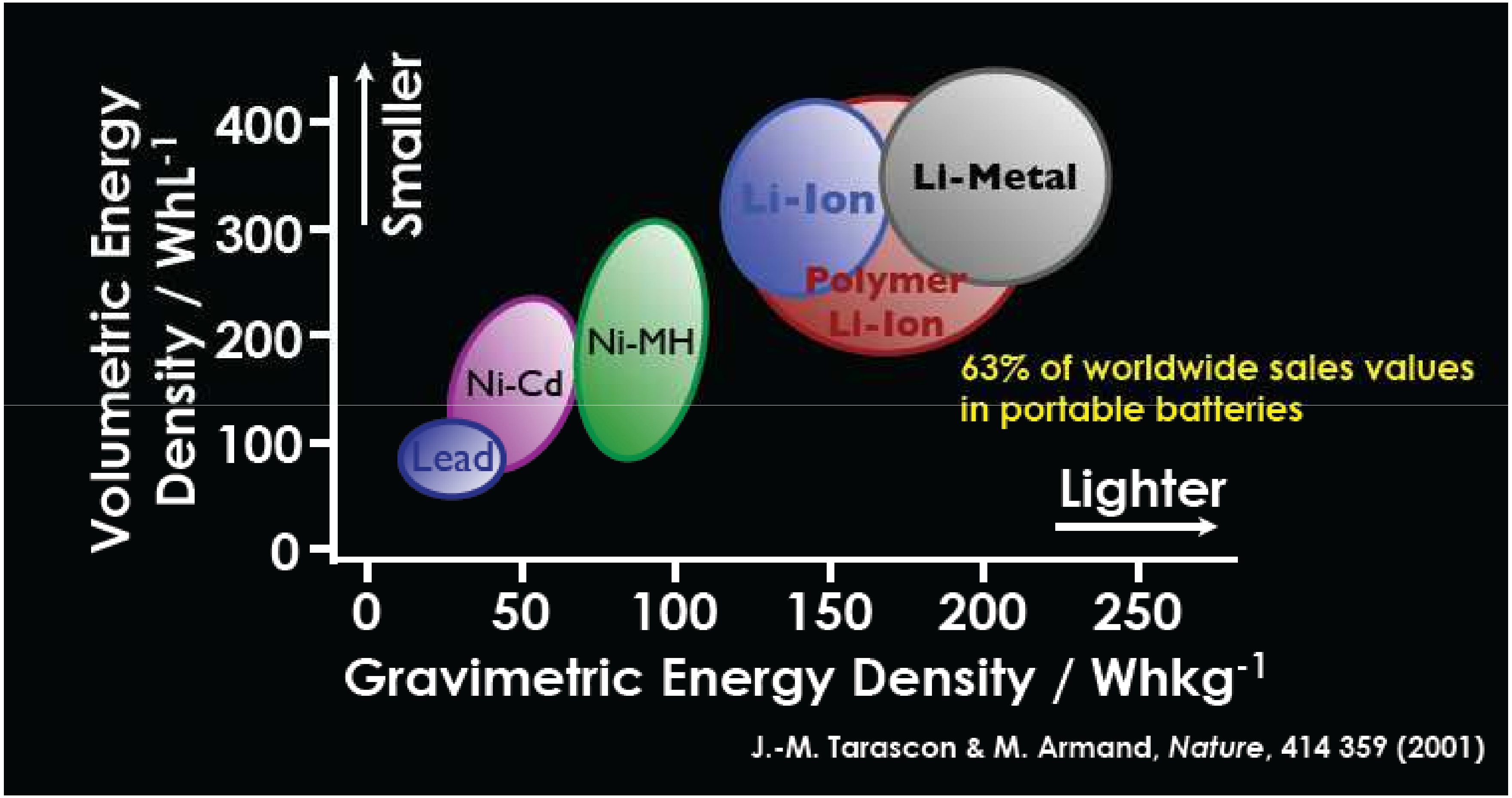
34% Petrolelum and 40% CO_2 emissions
Gasoline 13.000 Wh/kg (1700 Wh/kg)

Capacity 125 kWh for 250 Wh/miles
500 miles/800 kilometers

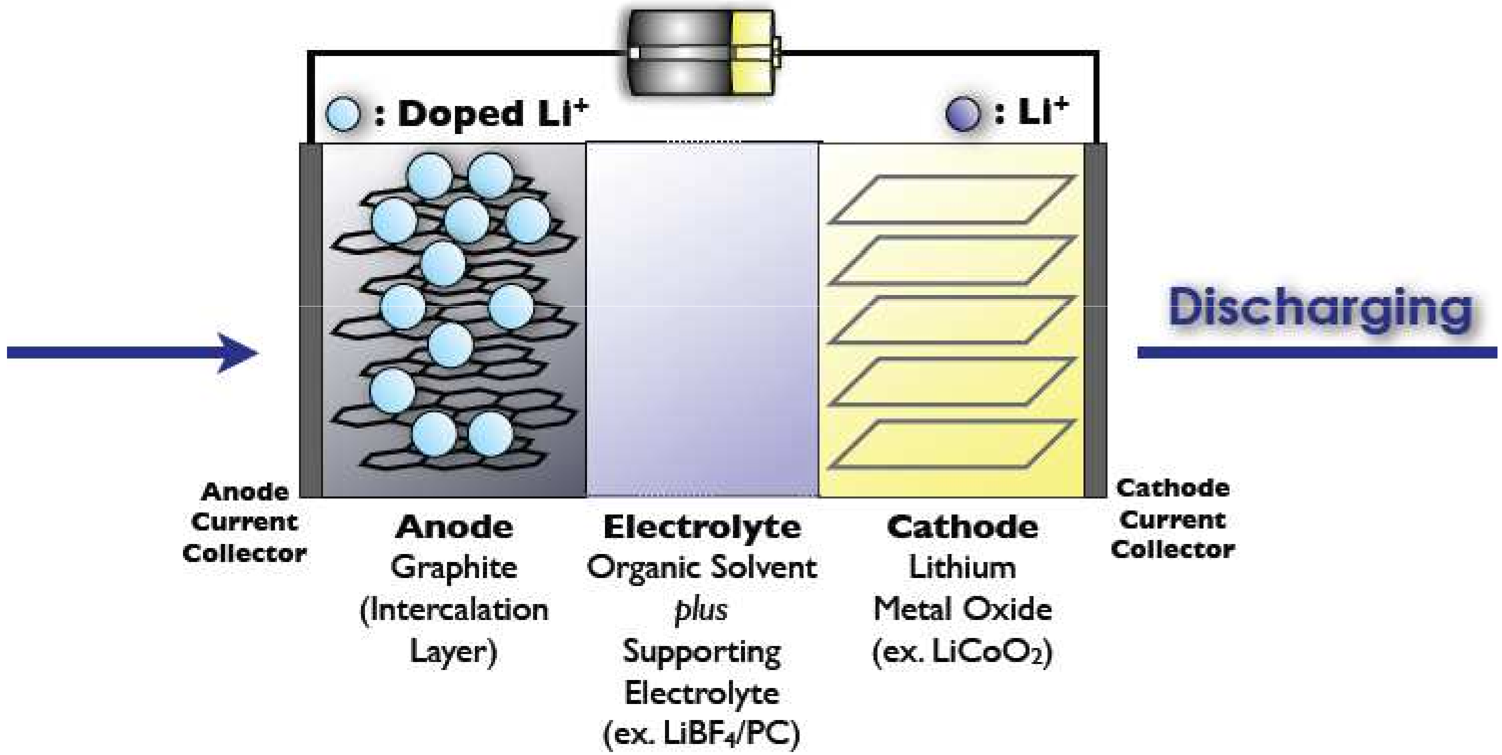
$2Li+O_2 = Li_2O_2$ 11.680 Wh/kg



"I LOVE my new CLEAN fuel cell car!"

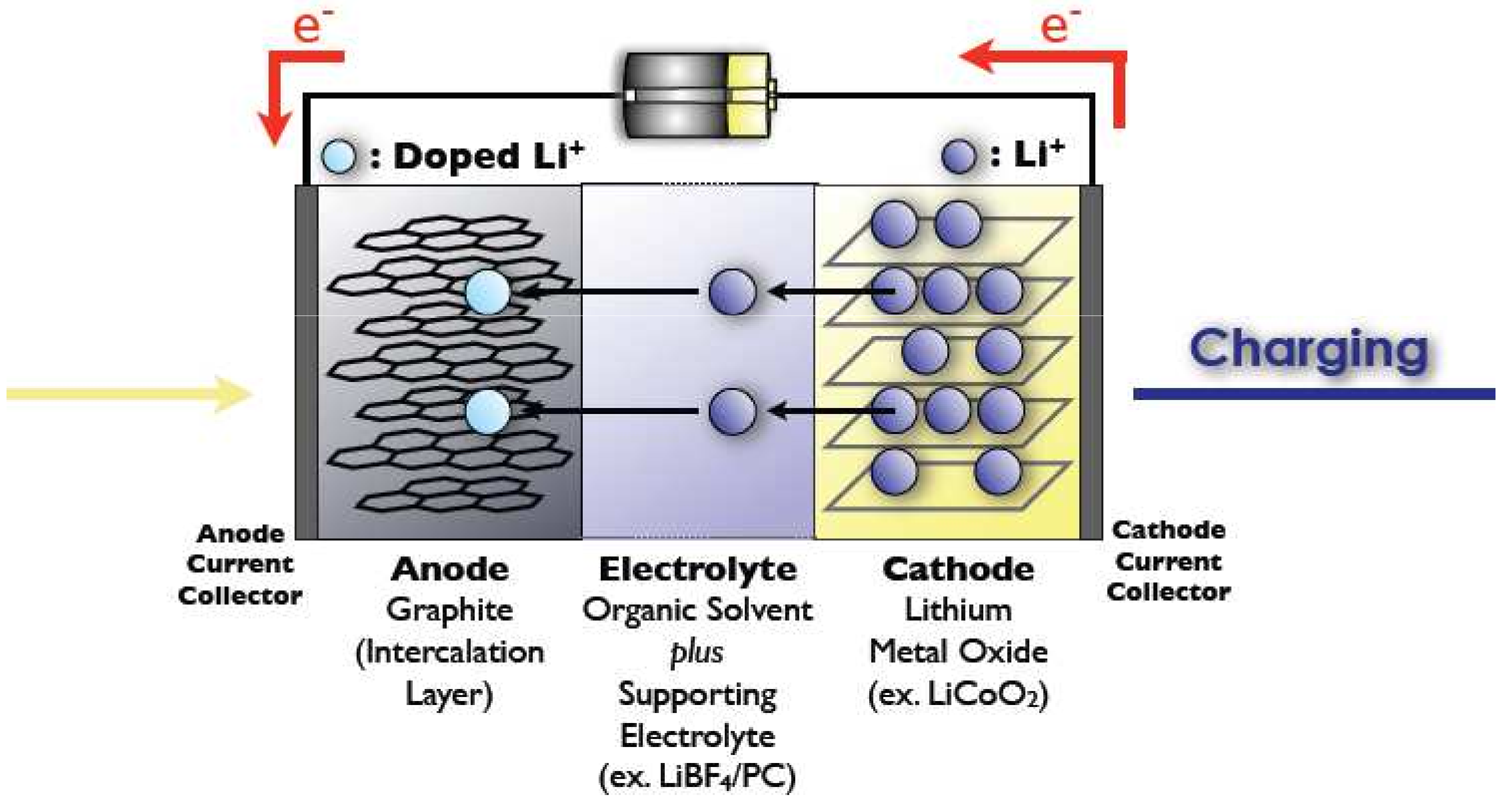

Volumetric Energy Density / WhL-1
Smaller
400
300
200
100
0
Lead
Ni-Cd
Ni-MH
Li-Ion
Polymer Li-Ion
Li-Metal
63% of worldwide sales values in portable batteries
Lighter
0
50
100
150
200
250
Gravimetric Energy Density / Whkg-1
J.-M. Tarascon & M. Armand, Nature, 414 359 (2001)

Fully Charged State

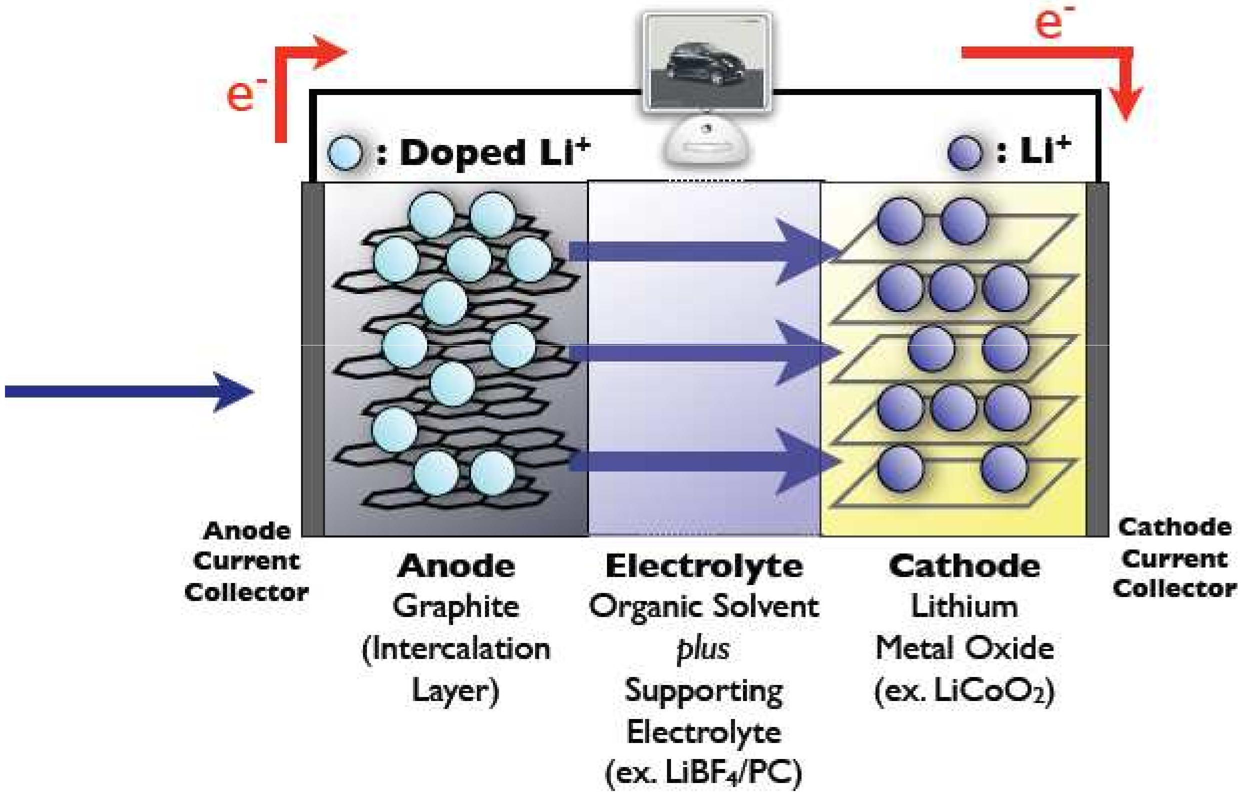


Mechanism of Lithium-ion Batteries

rocking chair



Fully Discharged State



OBJECTIVE FOR ELECTRIC VEHICLES

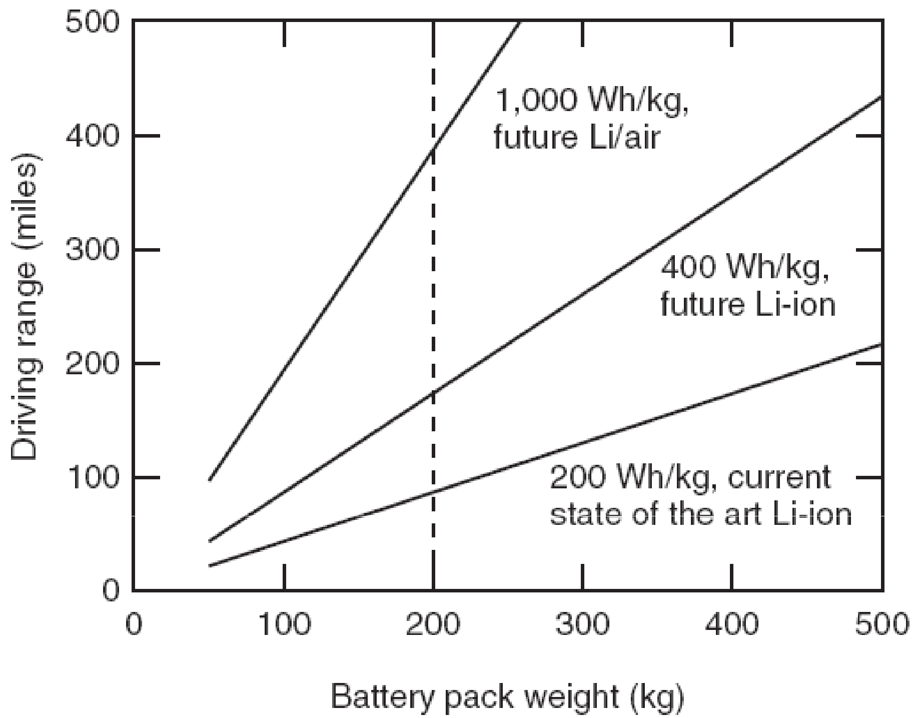
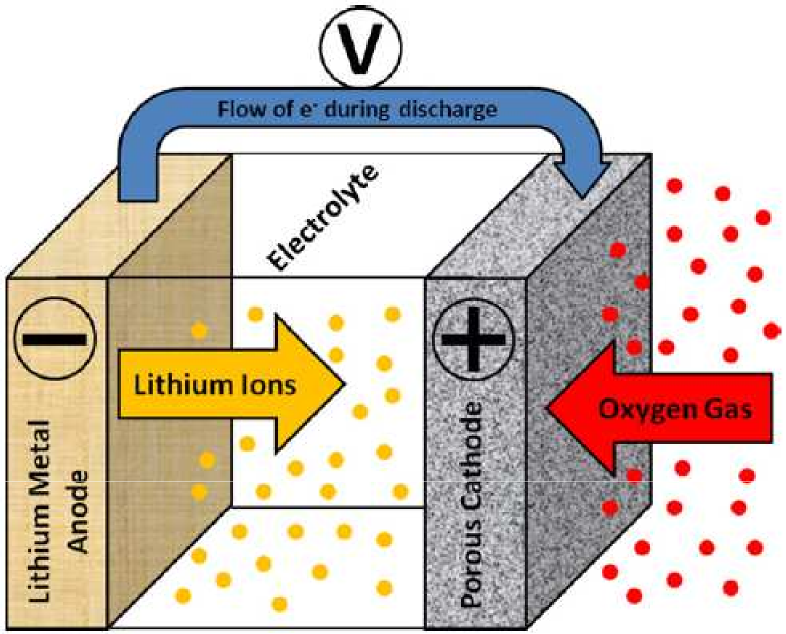


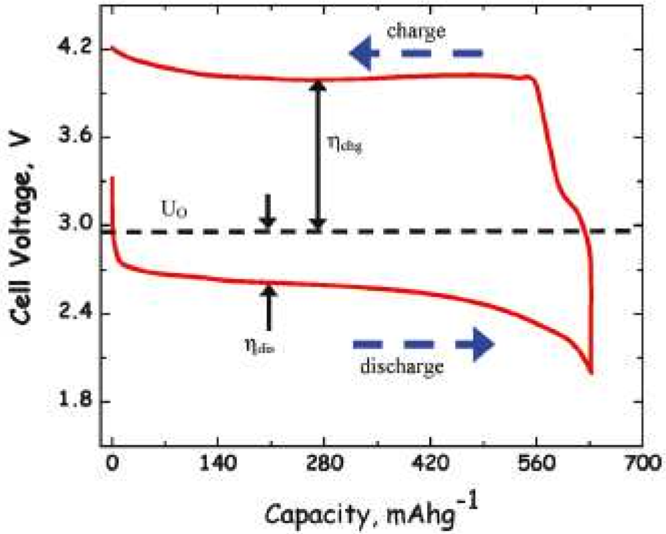
Figure 1. Driving range and battery weight for different cell-level specific energy values. It is assumed the battery cells weigh 70% of the battery pack, the Li/air cell has an 83% energy efficiency, the Li-on cells have a 93% energy efficiency, and 300 Wh/mile are required from the battery. The range 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)***

Lithium Air Rechargeable Batery





$$2Li + O_2 \rightarrow Li_2O_2$$

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

Anode

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

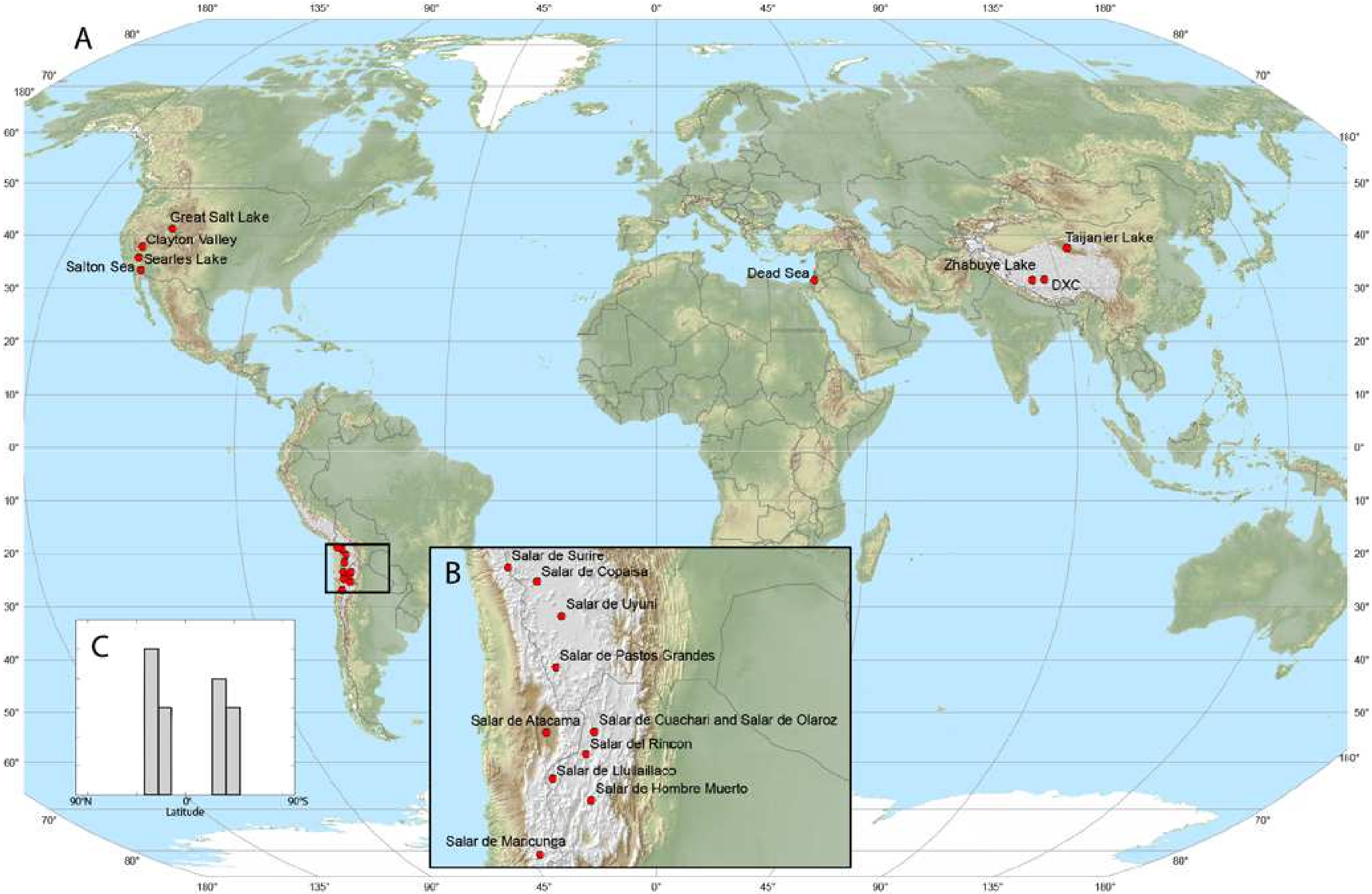
Cathode

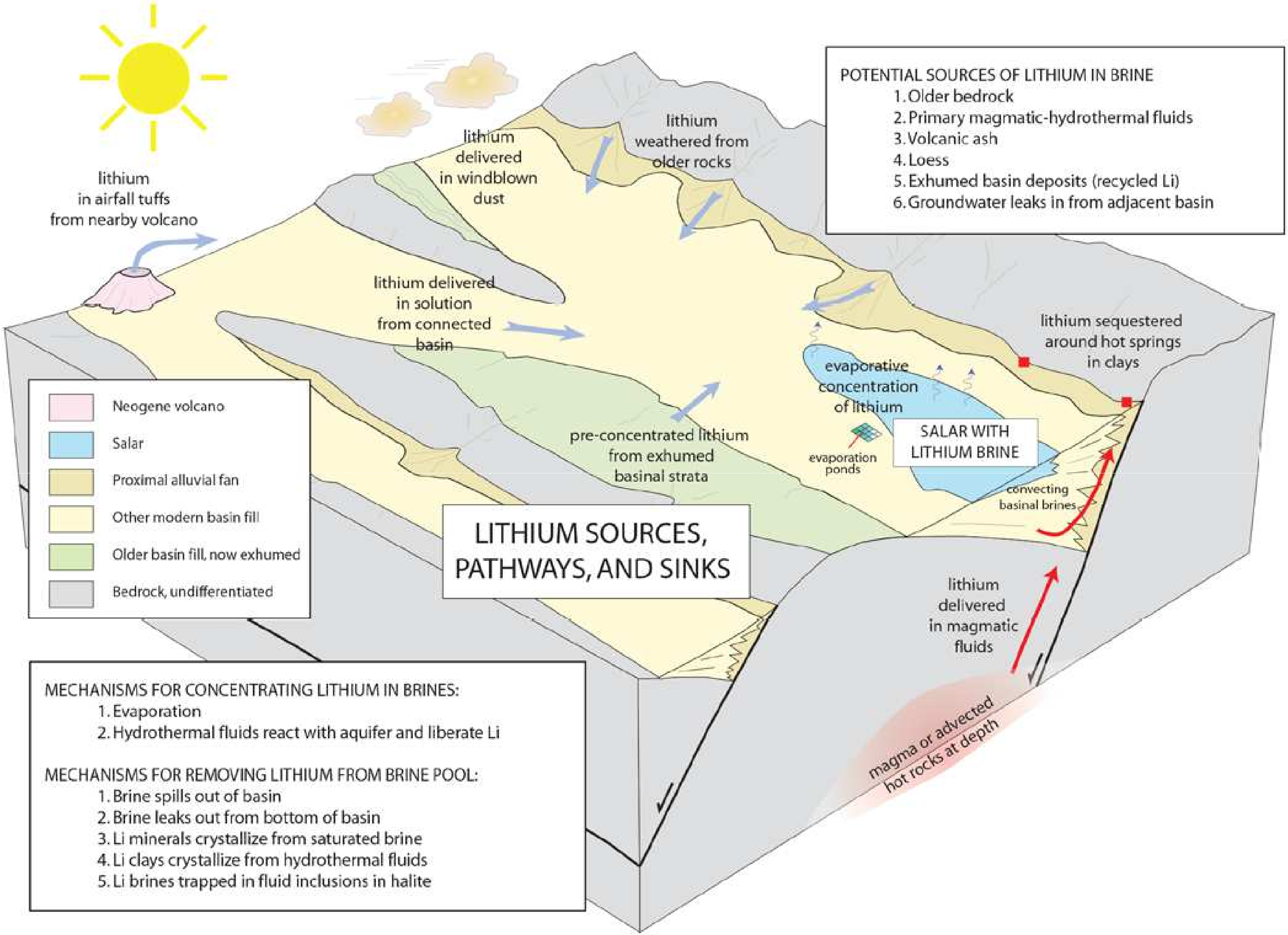
$$2(Li^+ + e^-) + O_2 \leftrightarrow Li_2O_2(\text{solid})$$

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

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

WORLD MAP OF LITHIUM RESOURCES





POTENTIAL SOURCES OF LITHIUM IN BRINE
1. Older bedrock
2. Primary magmatic-hydrothermal fluids
3. Volcanic ash
4. Loess
5. Exhumed basin deposits (recycled Li)
6. Groundwater leaks in from adjacent basin
lithium in airfall tuffs from nearby volcano
lithium delivered in windblown dust
lithium weathered from older rocks
lithium delivered in solution from connected basin
lithium sequestered around hot springs in clays
evaporative concentration of lithium
SALAR WITH LITHIUM BRINE
evaporation ponds
pre-concentrated lithium from exhumed basinal strata
connecting basinal brines
Neogene volcano
Salar
Proximal alluvial fan
Other modern basin fill
Older basin fill, now exhumed
Bedrock, undifferentiated
LITHIUM SOURCES, PATHWAYS, AND SINKS
lithium delivered in magmatic fluids
magma or advected hot rocks at depth
MECHANISMS FOR CONCENTRATING LITHIUM IN BRINES:
1. Evaporation
2. Hydrothermal fluids react with aquifer and liberate Li
MECHANISMS FOR REMOVING LITHIUM FROM BRINE POOL:
1. Brine spills out of basin
2. Brine leaks out from bottom of basin
3. Li minerals crystallize from saturated brine
4. Li clays crystallize from hydrothermal fluids
5. Li brines trapped in fluid inclusions in halite

SALT LAKES AT PUNA NORTH WEST ARGENTINA

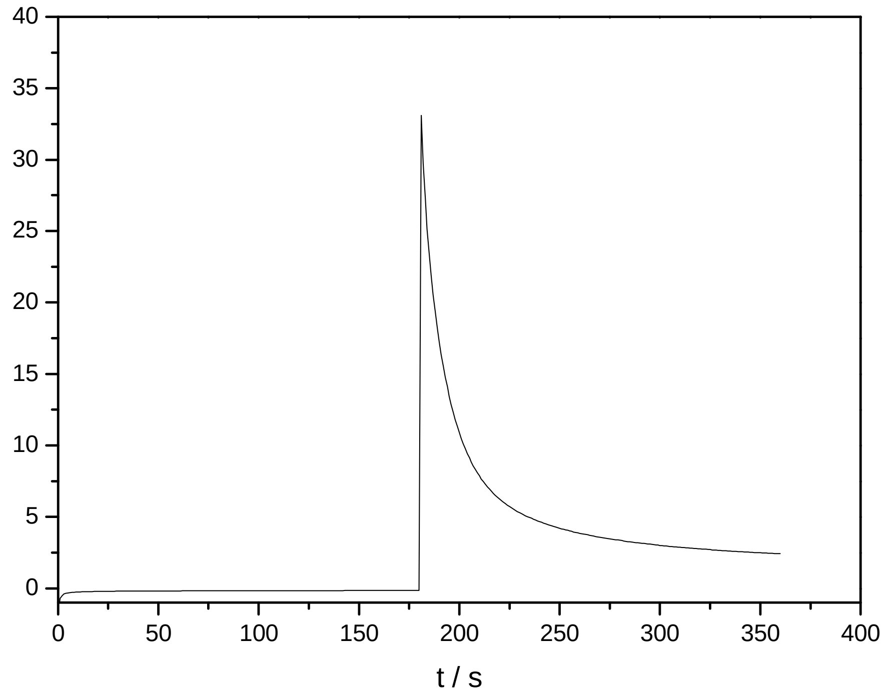
Electronic Acknowledgement Receipt	
EFS ID:	13787317
Application Number:	61702985
International Application Number:	
Confirmation Number:	1853
Title of Invention:	METHOD AND ELECTROCHEMICAL DEVICE FOR LOW ENVIRONMENTAL IMPACT LITHIUM RECOVERY FROM AQUEOUS SOLUTIONS
First Named Inventor/Applicant Name:	Ernesto Julio CALVO
Customer Number:	26111
Filer:	Jaime M. Canaves/Marianne Wood
Filer Authorized By:	Jaime M. Canaves
Attorney Docket Number:	3181.0020000/EJH/JCA
Receipt Date:	19-SEP-2012
Filing Date:	
Time Stamp:	16:29:12
Application Type:	Provisional

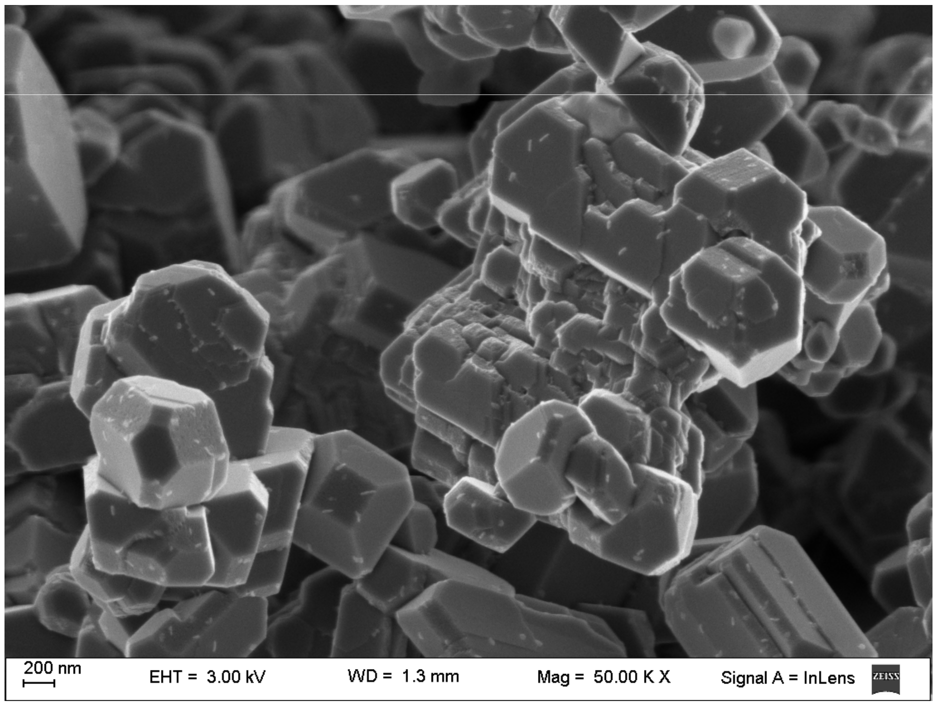
Lithium Recovery from Salt lakes brines with low environment impact

LITHIUM CAPTURE FROM BRINE

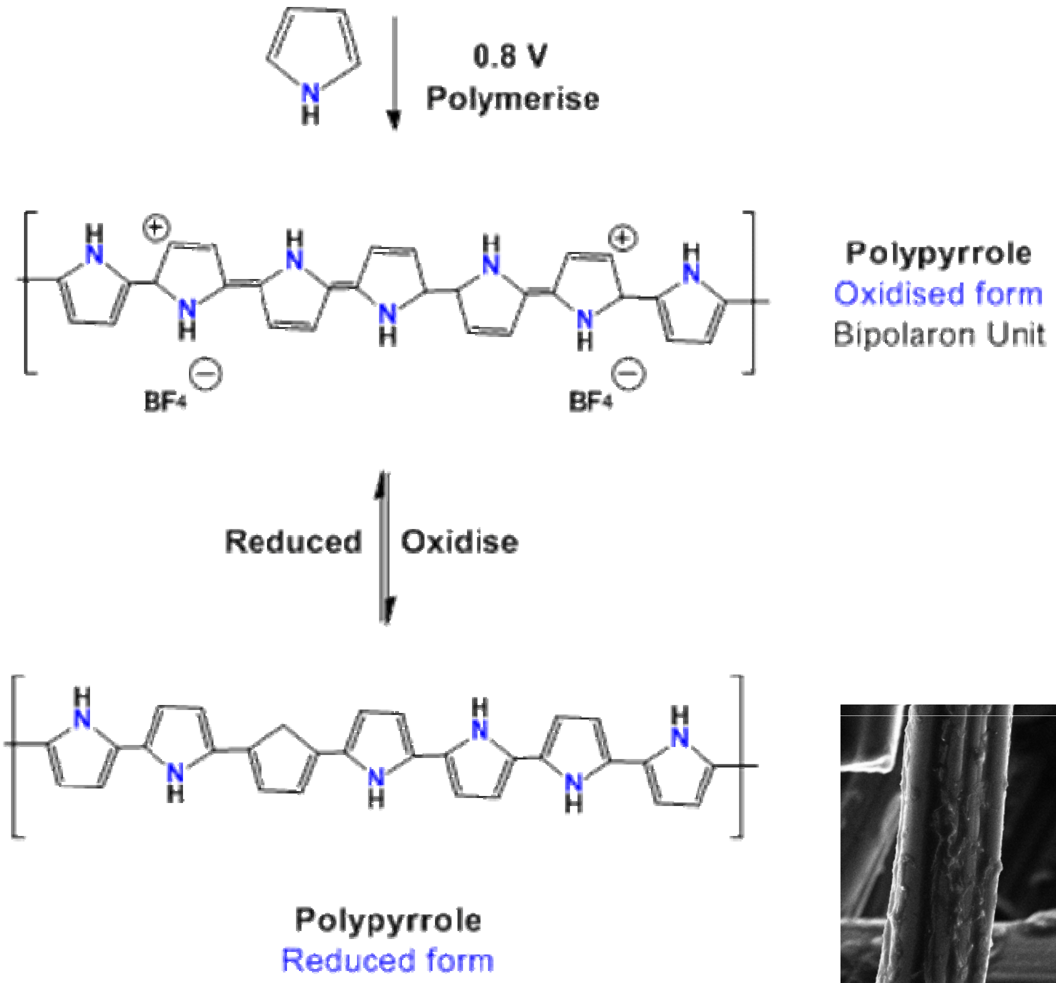
$$Li^{+} + Mn_{2}^{IV}O_{4} + e \rightleftarrows LiMn^{III}Mn^{iv}O_{4}$$

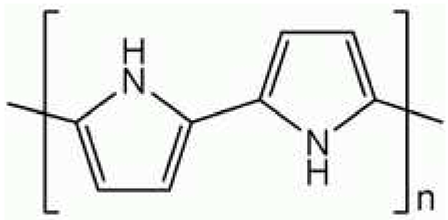
$$LiMn^{III}Mn^{IV}O_{4} \rightleftarrows Li^{+} + Mn_{2}^{IV}O_{4}(MnO_{2}) + e$$

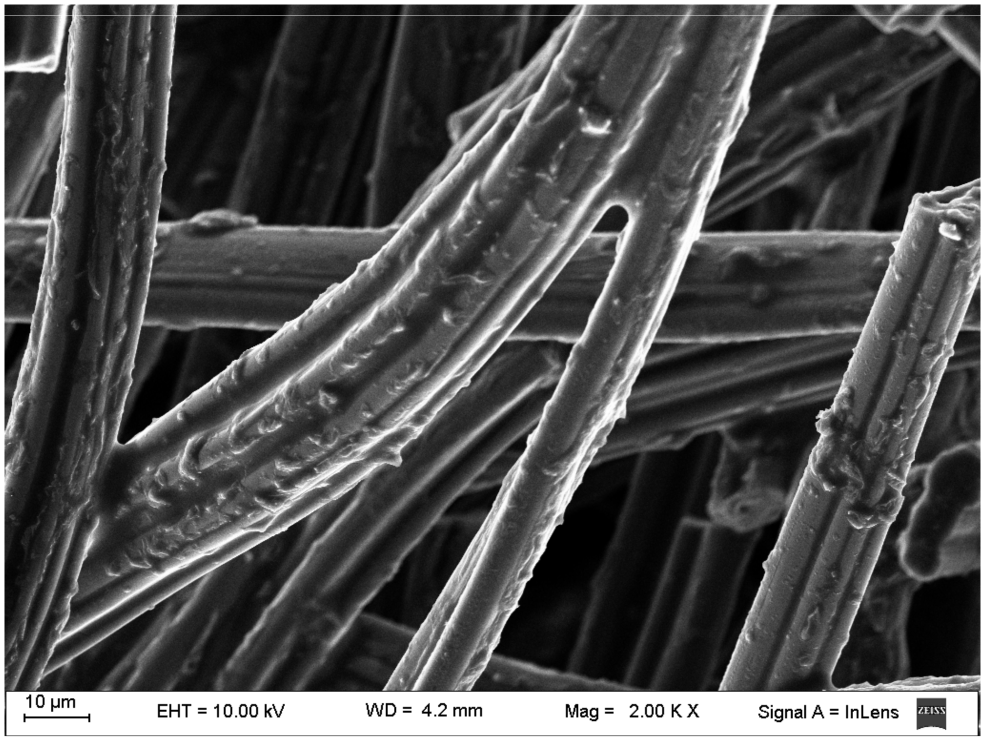




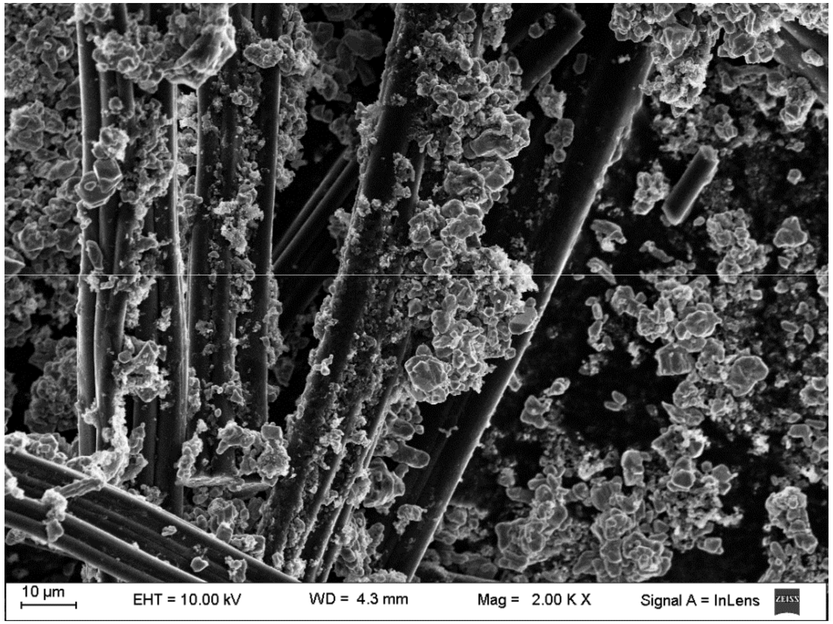
CHLORIDE CAPTURE

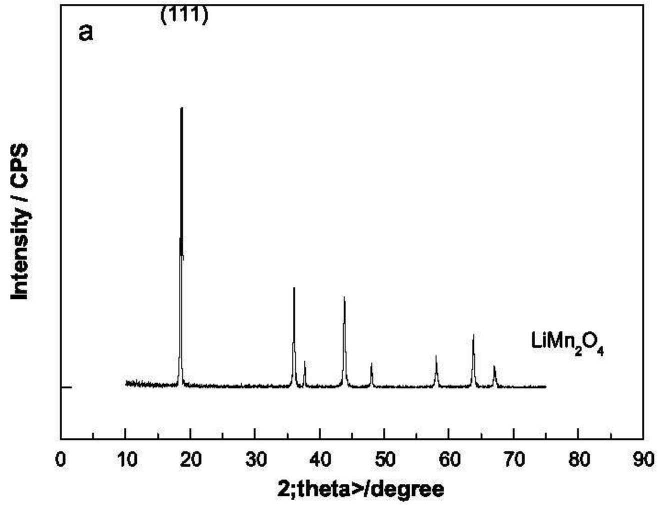


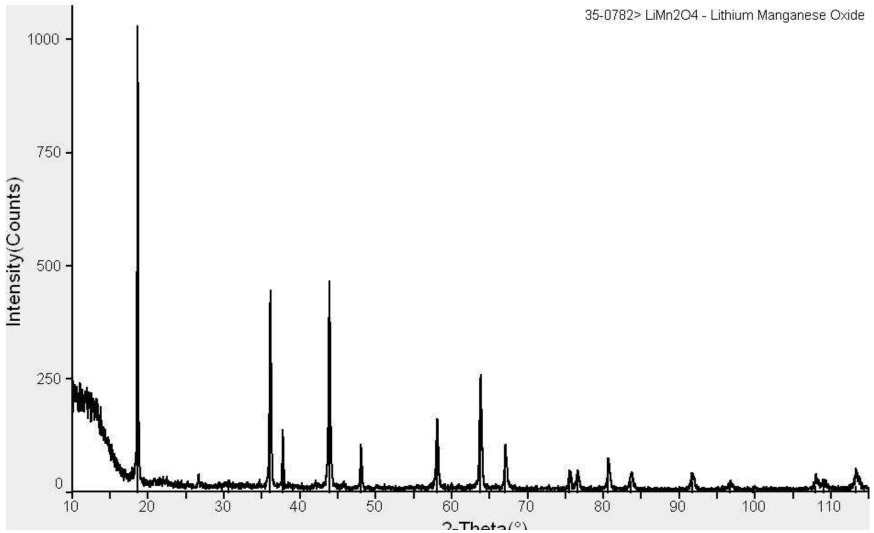


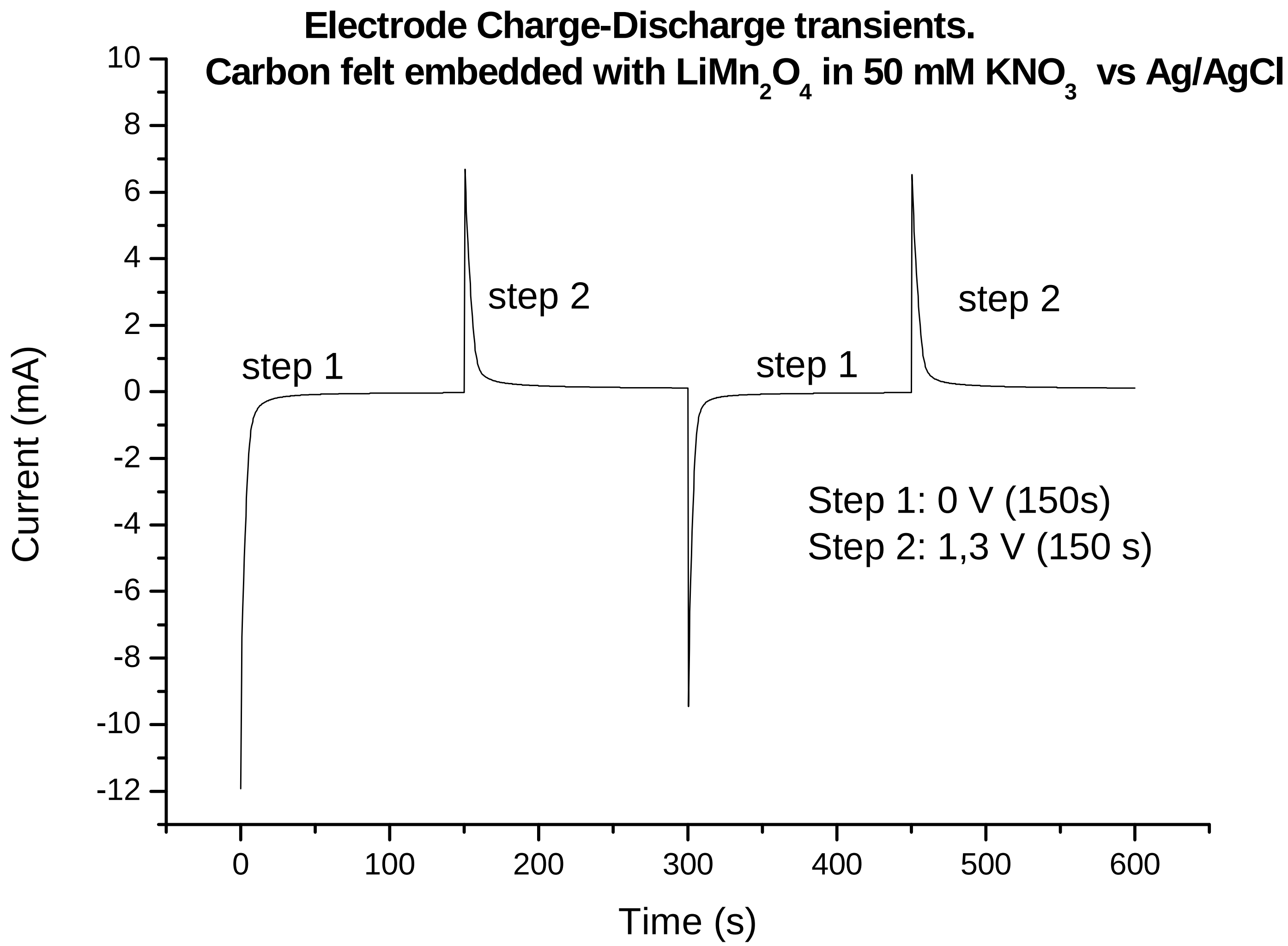


$LiMn_2O_4$ CRYSTALS ON CARBON FELT FIBERS

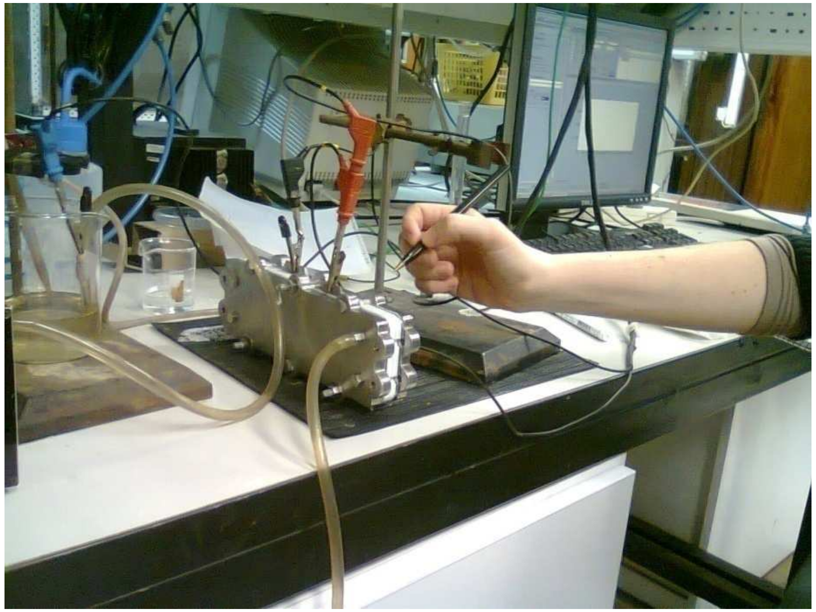


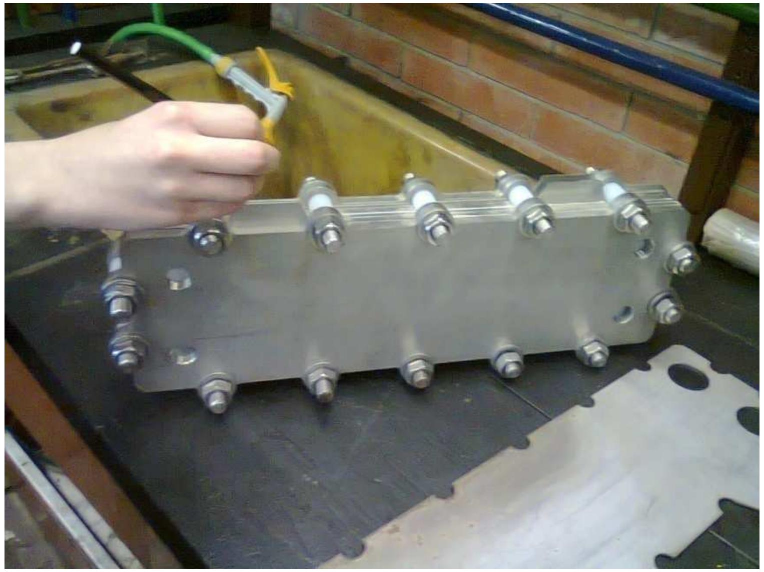


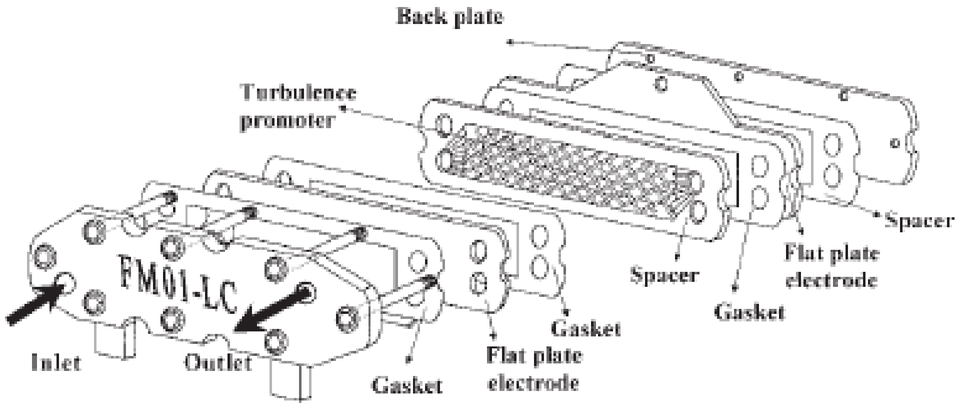


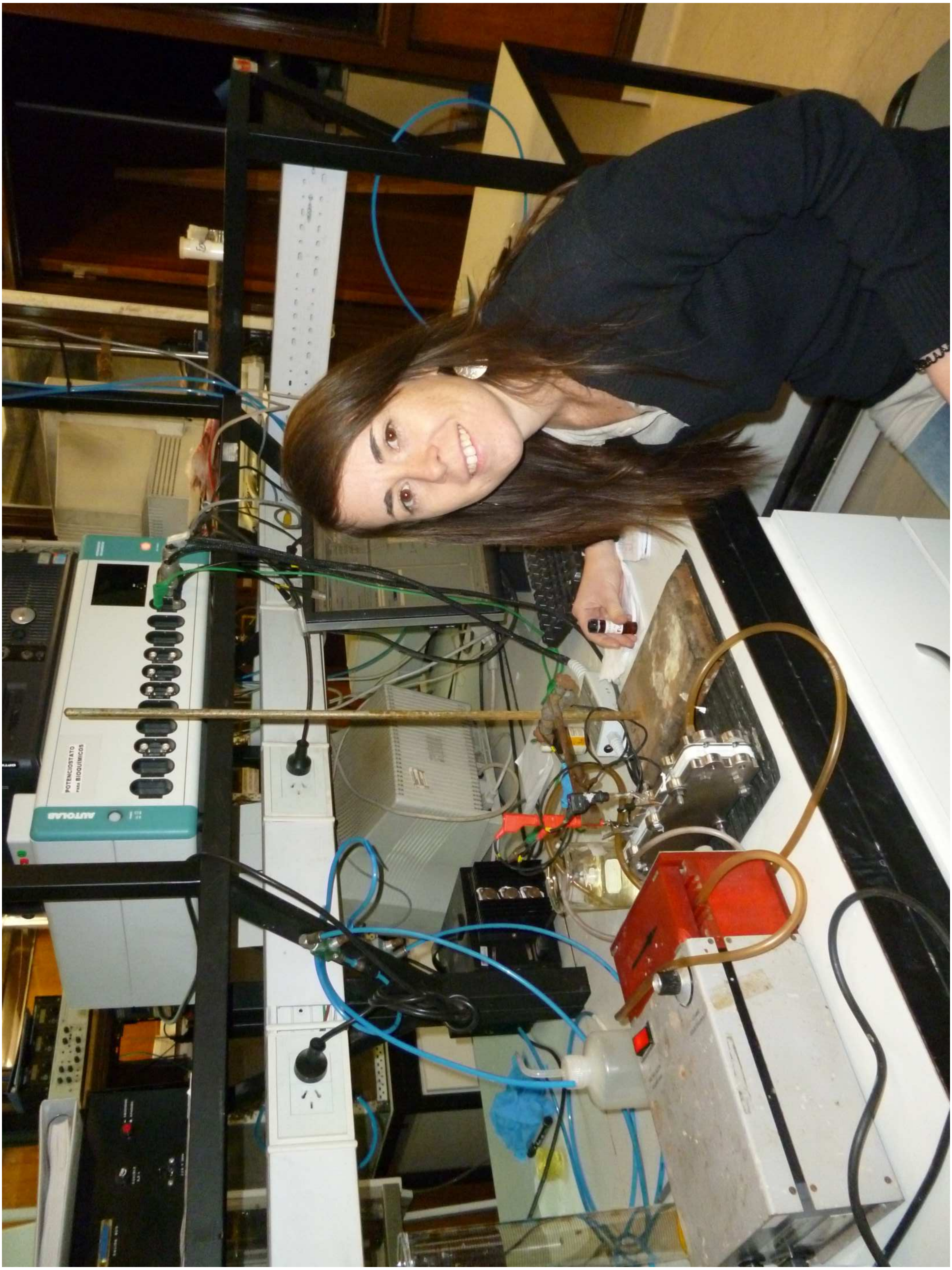

Electrode Charge-Discharge transients.
Carbon felt embedded with LiMn2O4 in 50 mM KNO3 vs Ag/AgCl
Current (mA)
10
8
6
4
2
0
-2
-4
-6
-8
-10
-12
step 1
step 2
step 1
step 2
Step 1: 0 V (150s)
Step 2: 1,3 V (150 s)
0
100
200
300
400
500
600
Time (s)

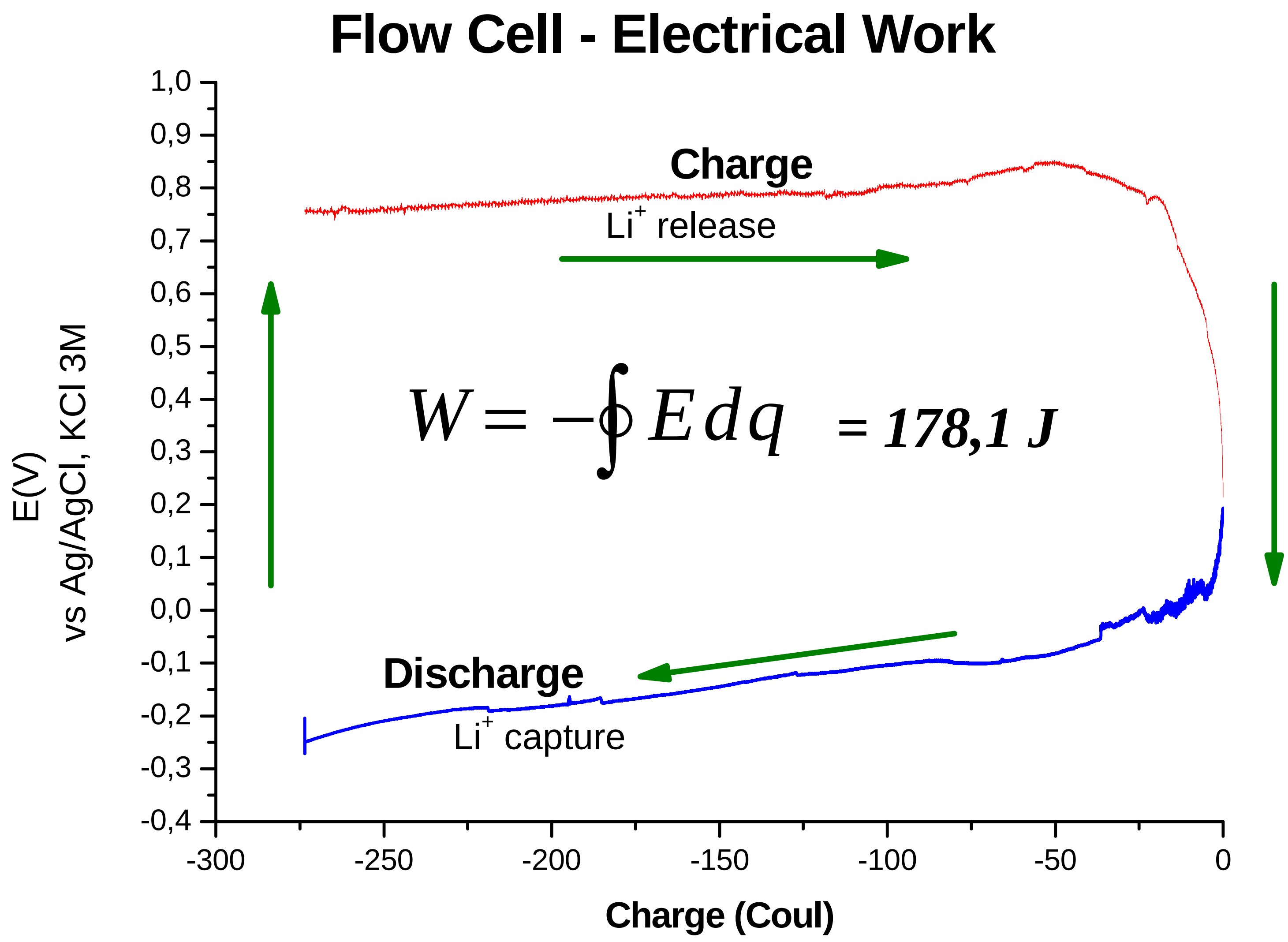
Press Filter Cell type FM01





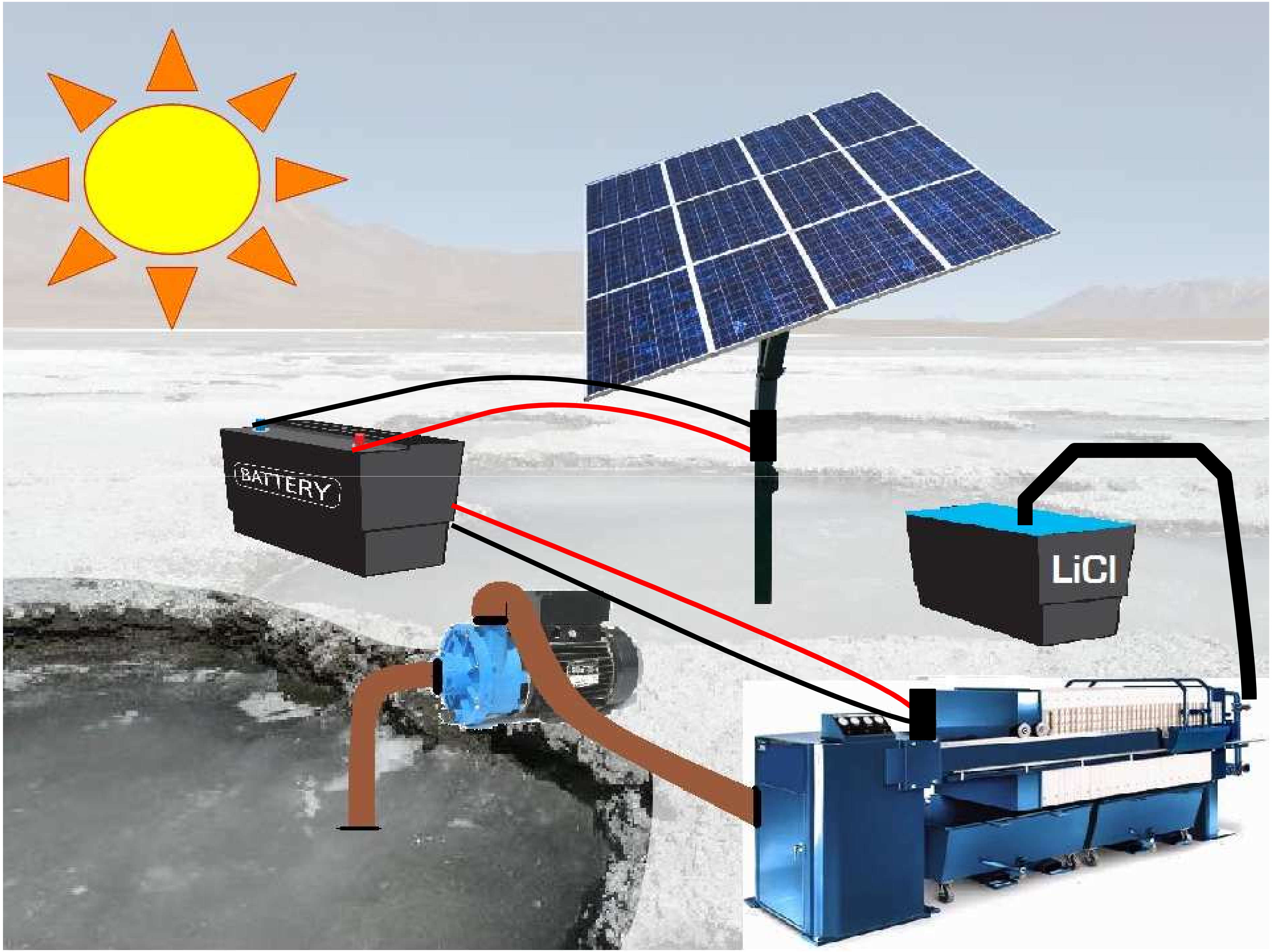



POTENCIOSTATO PARA BIOQUIMICOS
AUTOLAB



Flow Cell - Electrical Work
Charge
Li+ release
$$W = -\oint E\,dq$$
= 178,1 J
Discharge
Li+ capture
E(V)
vs Ag/AgCl, KCl 3M
Charge (Coul)
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
-0,1
-0,2
-0,3
-0,4
-300
-250
-200
-150
-100
-50
0

0,2 Wh/Kg

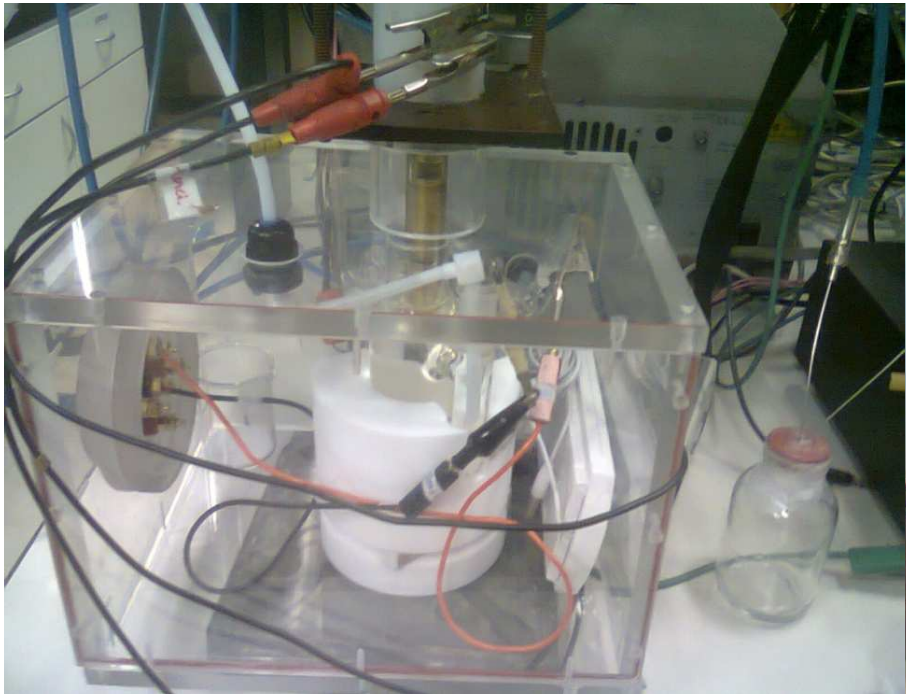

BATTERY
LiCl

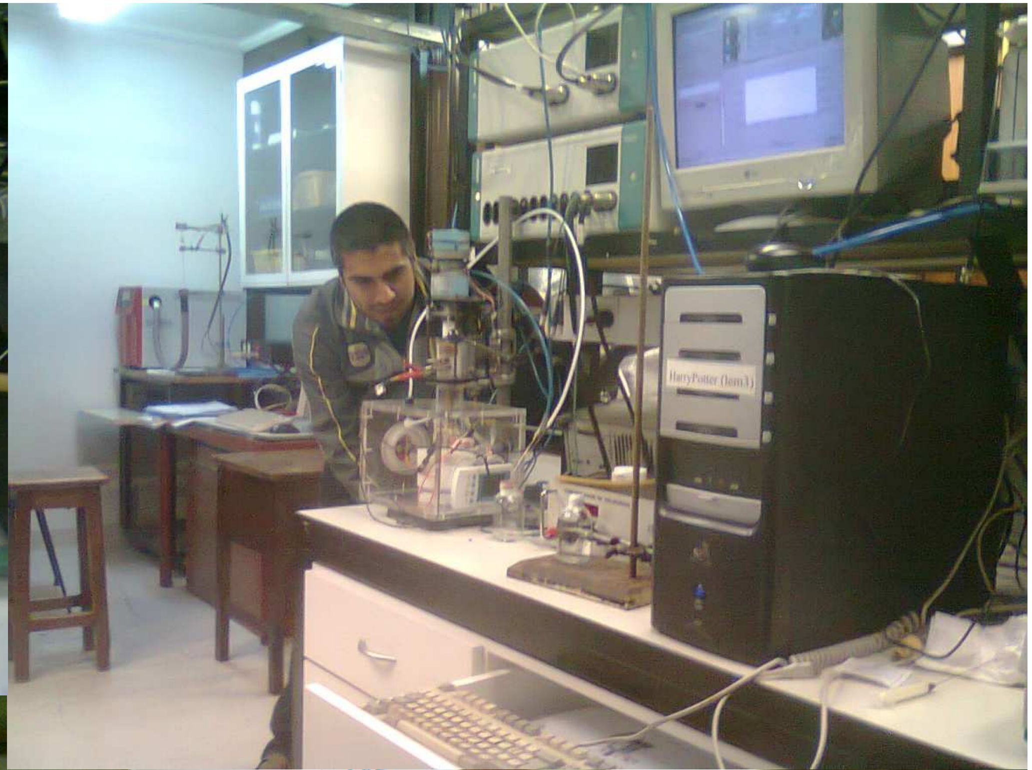
ENERGY COST

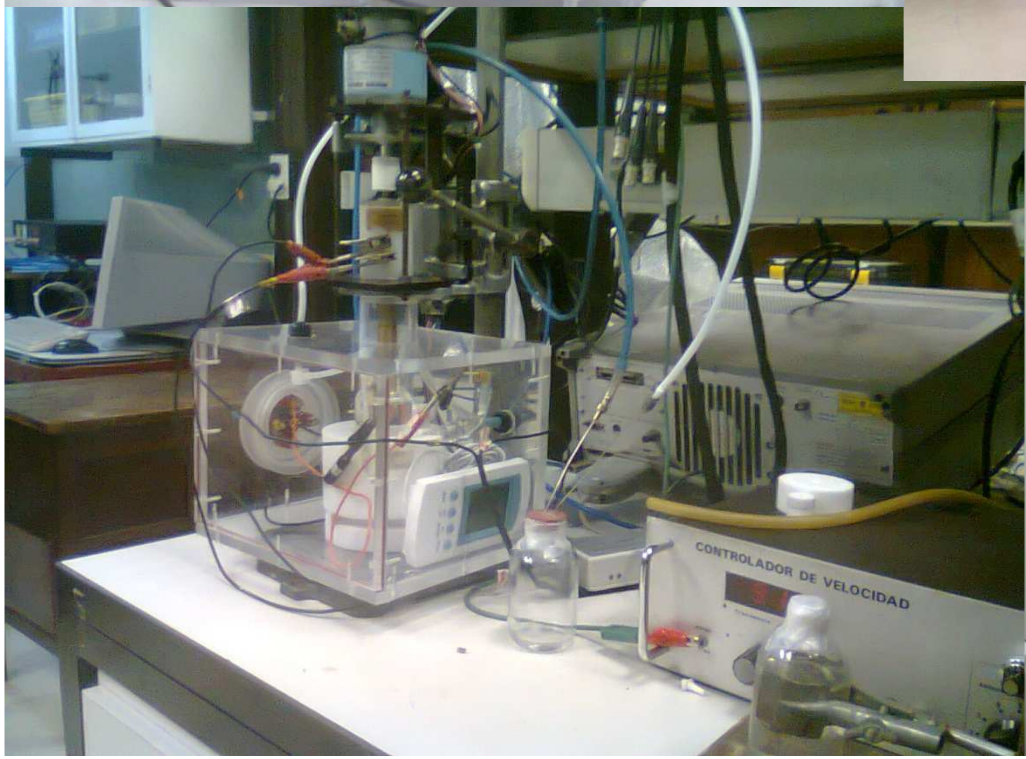
- 200 Kwh/ton of Li
- Solar Panels 2000 $us/ kW
- 50 kW $\rightarrow$200 kWh/day$\rightarrow$1 Ton Li/day
- Inversion 100.000 $us $\rightarrow$800 m^2 $\rightarrow$ 30 years life $\rightarrow$11.000 Ton
  - 10 $us/ton!!

Advantages of Method

- Clean,no consumtion of water, $Ca(OH)_2$, Na_2CO_3
- Low energy cost (200 kWh/ton).
- Fast (hours vs. months evaporation)
- Selective (Na^+ or Mg^{2+} interferences)
- Produces battery grade LiCl in a single step.




HarryPotter (lem3)


CONTROLADOR DE VELOCIDAD


LABmaster sp
BRAUN

CONCLUSIONS

• Chemistry plays a key role in materials, energy and environment. But we need sustainable chemistry friendly with our environment.

• We need to develop chemistry to extract minerals with minimun environmental impact.

• In a post petroleum economy we need clean chemistry to produce fuels and feedstock (chemicals for farmaceuticals, fertilizers, polymers, etc.).

• Sun $\rightarrow$ Electricity $\rightarrow$ Fuels

• We need to develop stable catalysts and mass production from earth abundant resources

•Training young scientists and engineers is key to the future success. Human Resources.

• Promote international cooperation.

THANK YOU