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

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Remote Electrification (7.5 GWh market in South America)

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

<table>
<thead>
<tr>
<th>Year</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>2012</td>
<td>7%</td>
</tr>
<tr>
<td>2014</td>
<td>27%</td>
</tr>
<tr>
<td>2016</td>
<td>50%</td>
</tr>
<tr>
<td>2026</td>
<td>1 TWh (1000 GWh)</td>
</tr>
</tbody>
</table>

Source: Roskill Report
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 store the energy of 17,000 cell phones
Tesla plans to manufacture 500,000 electric cars in 2018 (aprox. 2.250 ton of lithium)
Las baterías almacenan energía en compuestos químicos capaces de generar carga eléctrica.
- Poseen alta densidad de energía.
- Existe una gran variedad de baterías.

**Baterías Primarias (No recargables)**
- Zn/carbon 1,5 V, 0,13
- Zinc/aire 1,4 V
- Zn/MnO₂ (alcalinas), 1, 5 V
- Li/O₂, 2,91 V
- Li-SOCl₂, 3,5 V

**Baterías Secundarias (Recargables)**
- PbO₂/PbSO₄, 2,1 V
- Ni/Cd, 1,2 V
- Ni/MHₓ (AA), 1,2 V, 1,3 Ah
- C₆Liₓ/LiCoO₂, 3,7 V
- Li/LiFePO₄, 3,3 V
- Li/O₂, 2,91 V (futuro para vehículos)
Can we extract lithium at a large scale in a sustainable way?
Baterías de ion litio (sony 1991)

LiCoO₂ ↔ Li_{1-x}CoO₂ + xLi⁺ + xe⁻

Cathode

+C + xLi⁺ + xe⁻ ↔ LiₓC

Anode

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

Ion diffusion : Interfaces
→ Particle size and NANO
Anode and Cathode Materials: Possibilities

Cathode materials:
Lithium/Li-ion

- \( \text{xLi}_2\text{MnO}_3/(1-\text{x})\text{LiMO}_2 \) (M = Mn, Ni, Co, Cr)
- LiMnPO_4, LiCoPO_4, LiNiPO_4
- Li_{2-x}M_{x}O, Li_{4-x}M_{x}O (M=Fe, Co)
- LiNiVO_4, LiNi_{0.5}Mn_{0.5}O_2

Anode materials:
Lithium/Li-Ion

- Li_{4}Ti_{5}O_{12}
- Graphite
- Carbons
- Sn
- Metal oxides (displacement-type)
- Si/C composites
- Li metal
- Si

Potential vs. Li/Li^+

Capacity / Ah kg^{-1}
Cathode Materials

Intercalation compounds
John Goodenough, 1980’s

LiFePO$_4$  LiCoO$_2$  TiS$_2$

VO$_2$  YBa$_2$Cu$_3$O$_7$  WO$_3$

Figure 3.3: Cross-section of a prismatic cell.
Effects of Nanoparticle Geometry and Size Distribution on Diffusion Impedance of Battery Electrodes

Juhyun Song\textsuperscript{a} and Martin Z. Bazant\textsuperscript{a,b,\dagger,\ddagger}

\textsuperscript{a}Department of Chemical Engineering and \textsuperscript{b}Department of Mathematics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

\[ \frac{\partial c}{\partial t} = D_{ch} \nabla^2 c \quad \quad \hat{j}_{intc} = -eD_{ch} \frac{dc}{dx} \bigg|_{x=l} \]

LiCoO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, LiFePO\textsubscript{4}

D\textsubscript{Li\textsuperscript{+}} = 10^{-8} \text{ – } 10^{-10} \text{ cm}^2\text{.s}^{-1}

\[ \frac{l^2}{D_{Li\textsuperscript{+}}} = \tau \]

Distancia difusional característica:

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

Para l = 10^{-4} \text{ cm (1 \text{ \mu m})} \quad \tau = 100 \text{ seg}

Para l = 10^{-5} \text{ cm (100 \text{ nm})} \quad \tau = 1 \text{ seg}

Para l = 10^{-6} \text{ cm (10 \text{ nm})} \quad \tau = 0,01 \text{ seg}

\textbf{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.
Recent advances in LiFePO₄ nanoparticles with different morphology for high-performance lithium-ion batteries

\[ x\text{Li}^+ + x\text{e}^- + \text{MPO}_4 \leftrightarrow \text{LiMPO}_4 \ (\text{M} = \text{Fe, Mn, Co, Ni}) \]

- LiFePO₄: 3.5V
- LiMnPO₄, LiMn₀.8Fe₀.2PO₄: 4.1V
- LiCoPO₄: 4.8V

10 nm C Nanocoating

Fig. 3 Schematic models for lithium extraction/reinsertion into a single particle of a LiFePO₄ radial model (a) and Mosaic model (b).⁹⁹

Fig. 4 (a) Electron-transfer pathway for LiFePO₄ particles partially coated with carbon. (b) Designed ideal structure for LiFePO₄ particles with typical nano-size and a complete carbon coating.⁹⁹
Anodos para baterías recargables de ion litio

Sn + xe⁻ + xLi⁺ ⇄ LiₓSn ; x → 4.4 > 900 mAh/g
Si + xe⁻ + xLi⁺ ⇄ LiₓSi ; x → 4.4 > 4000 mAh/g

Problem! Nano structures are required

Insertion

MX₂ + e⁻ + Li⁺ ⇄ + LiMX₂

Conversion

MX + 2e⁻ + 2Li⁺ ⇄ M + Li₂X

Sn + xe⁻ + xLi⁺ ⇄ LiₓSn ; x → 4.4 > 900 mAh/g
Si + xe⁻ + xLi⁺ ⇄ LiₓSi ; x → 4.4 > 4000 mAh/g

Problem! Nano particles are required

En la actualidad
Intercalation compounds

Titanium Oxide
Li₄Ti₅O₁₂ + 3Li⁺ + 3 e⁻ ↔ Li₇Ti₂O₁₂
Practical capacity = 160 mAhg⁻¹

Graphite
Li₁₋ₓC₆ + xLi⁺ + e⁻ ↔ LiC₆
Practical capacity = 330 mAhg⁻¹
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

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).
Porous silicon nanowires for lithium rechargeable batteries

Jung-Keun Yoo¹, Jongsoon Kim², Hojun Lee¹, Jaesuk Choi¹, Min-Jae Choi¹, Dong Min Sim², Yeon Sik Jung¹,³ and Kisuk Kang²,³

Figure 2. SEM images of (a) as-spun TEOS/PVP nanowires, (b) SiO₂ 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).
Yolk–Shell Structure of Polyaniline-Coated Sulfur for Lithium–Sulfur Batteries

Weidong Zhou,†,* Yangchao Yu,† Hao Chen,† Francis J. DiSalvo,† and Héctor D. Abrau†,*

†Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, USA.

Supporting Information

Cathode

S\textsubscript{8} \rightarrow Li\textsubscript{2}S\textsubscript{8} \rightarrow Li\textsubscript{2}S\textsubscript{6} \rightarrow Li\textsubscript{2}S\textsubscript{4} \rightarrow Li\textsubscript{2}S\textsubscript{3}

Anode

Li\textsubscript{2}S \rightarrow Li\textsubscript{2}S\textsubscript{2} \rightarrow Li\textsubscript{2}S\textsubscript{3} \rightarrow Li\textsubscript{2}S\textsubscript{4} \rightarrow Li\textsubscript{2}S\textsubscript{6} \rightarrow Li\textsubscript{2}S\textsubscript{8} \rightarrow S\textsubscript{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

LITHIUM PRODUCTION COSTS BY SOURCE

Source: Roskill, company reports, UBS estimates

Source: Roskill, UBS. NB: Brines are 2015 costs, mineral concentrate plants in China using 2017 spodumene contract prices.
Salar Hombre Muerto. FMC
Catamarca, Argentina
## CHEMICAL COMPOSITION OF BRINES FROM SALT FLATS

<table>
<thead>
<tr>
<th></th>
<th>Atacama</th>
<th>Uyuni</th>
<th>Hombre Muerto</th>
<th>Cauchari</th>
<th>Olaroz</th>
<th>Rincón</th>
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<tr>
<td>Na</td>
<td>7,60</td>
<td>8,75</td>
<td>9,79</td>
<td>9,55</td>
<td>9,46</td>
<td>9,46</td>
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<tr>
<td>K</td>
<td>1,85</td>
<td>2,72</td>
<td>0,617</td>
<td>0,47</td>
<td>0,656</td>
<td>0,66</td>
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<tr>
<td>Li</td>
<td>0,150</td>
<td>0,035</td>
<td>0,062</td>
<td>0,082</td>
<td>0,033</td>
<td>0,033</td>
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<tr>
<td>Mg</td>
<td>0,98</td>
<td>0,65</td>
<td>0,085</td>
<td>0,131</td>
<td>0,323</td>
<td>0,303</td>
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<tr>
<td>Ca</td>
<td>0,031</td>
<td>0,046</td>
<td>0,053</td>
<td>0,034</td>
<td>0,059</td>
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<tr>
<td>Cl</td>
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<td>15,69</td>
<td>15,80</td>
<td>14,86</td>
<td>18,06</td>
<td>16,06</td>
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<tr>
<td>SO₄</td>
<td>1,65</td>
<td>0,85</td>
<td>0,853</td>
<td>1,62</td>
<td>1,015</td>
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<td>B</td>
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<td>0,035</td>
<td>0,076</td>
<td>0,040</td>
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<tr>
<td>K/Li</td>
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<td>20,57</td>
<td>9,95</td>
<td>9,04</td>
<td>20,12</td>
<td>1,220</td>
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<tr>
<td>Na/Li</td>
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<td>250</td>
<td>158</td>
<td>116</td>
<td>286</td>
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<tr>
<td>Mg/Li</td>
<td>6,53</td>
<td>18,6</td>
<td>1,37</td>
<td>2,52</td>
<td>9,78</td>
<td>9,29</td>
</tr>
</tbody>
</table>
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 from Olaroz, Jujuy, Argentina.

Li: 1,3 g/L
Na: 62,6 g/L
Ca: 3,6 g/L
Mg: 3,3 g/L
K: 8,1 g/L
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


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


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

What is unique?

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

Premium Solar energy
Extract lithium chloride
Lithium batteries
Interrruptent renewable energy storage

Battery generates energy
Consumes energy


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

\[ \text{Li}^+ \rightarrow \text{LiCl} \rightarrow \text{Diluted LiCl} \]

\[ \text{Cl}^- \rightarrow \text{Diluted LiCl} \]
Dicharge of battery-reactor in Natural Brine to extract Lithium Chloride

Spontaneous Process

Brine

Lithium ion insertion, $R = 10 \, k\Omega$

Δ$E$ (V) vs. $Q$ (mC)

Lithium in insertion from Natural Brine Load $R=10K\Omega$

$\Delta E$ (V) vs. $Q$ (mC)
The spontaneous process on the left side (capture of LiCl from natural brine) feeds electrical charge into the right side reactor (release of LiCl)
Natural Brine Olaroz

- Insertion with load $R=10\,\Omega$
- Extraction at $i = 50\,\mu A$

Delitiation charge: 147 mC
Litiation charge: 125 mC
85% spontaneous recovery
Successful 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

WHERE WE WANT TO GO?
Bench Top Modelling
Electrochemical Engineering
Unit Process

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
A LiMn$_2$O$_4$-Polypryrrole System for the Extraction of LiCl from Natural Brine

Leandro L. Missoni, Florencia Marchini, María del Pozo, and Ernesto J. Calvo
INQUIMAE, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, AR-1428 Buenos Aires, Argentina

CATHEODGE Selective to Lithium

\[ x\text{Li}^+ (\text{brine}) + \text{Li}_{1-x}\text{Mn}_{1-x}\text{Mn}^{IV}_2\text{O}_2 + xe^- (\text{cathode}) \rightleftharpoons \text{LiMn}^{IV}\text{Mn}^{III}_2\text{O}_4 \]

ANODE Selective to Chloride

\[ x\text{Cl}^- (\text{brine}) + x\text{PP}^0 (\text{anode}) \rightleftharpoons x[\text{PP}^+\text{Cl}^-] + xe^- (\text{anode}) \]

OVERALL REACTION

\[ x\text{Li}^+ (\text{brine}) + x\text{Cl}^- (\text{brine}) + \text{Li}_{1-x}\text{Mn}_{1-x}\text{Mn}^{IV}_2\text{O}_2 + x\text{PP}^0 \rightleftharpoons \text{LiMn}^{IV}\text{Mn}^{III}_2\text{O}_4 + x[\text{PP}^+\text{Cl}^-] \]

By limiting the potential we avoid the reaction:

\[ \text{LiMn}^{IV}\text{Mn}^{III}_2\text{O}_4 + x\text{Li}^+ + xe^- \rightleftharpoons \text{Li}_{1+x}\text{Mn}^{III}_{1+x}\text{Mn}^{IV}_{1-x}\text{O}_4 \]

With two phase LiMn$_2$O$_4$ / Li$_2$Mn$_2$O$_4$ separation

Two-Step Process: LiCl capture and recovery
Pld deposited film

![Scanning Electron Microscope Image](image)

**Crystal Structure Analysis**

- **LMO**
- **Reference**

**Technical Details**

- **EHT**: 3.00 kV
- **WD**: 4.2 mm
- **Mag**: 250.00 K X
- **Signal A**: InLens

**Scale**

- 100 nm
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.
\[ a = 8.045 \text{ Å} \]
\[ a = 8.152 \text{ Å} \]
\[ x = 0.12 \]
\[ x = 0.75 \]
\[ x = 1 \]

**BULK CRYSTAL XRD**

**SURFACE XPS ANALYSIS**

**0.6 V, NaCl**

**\( x = 0.12 \)**

**\( x = 0.75 \)**

**\( x = 1 \)**

**Binding energy (eV)**

- 0.6 V
- 0.75 V
- 0.85 V
- 1.1 V

\[ \theta \text{ (degrees)} \]

\[ % \text{ Mn (IV)} \]

\[ E \text{ (V, vs Ag/AgCl)} \]
ELECTROCHEMICAL REACTOR

Li$_{1-x}$Mn$_2$O$_4$ (LMO) LITHIUM-ION POROUS ELECTRODE

POLYPYRROLE (PPy) CHLORIDE SELECTIVE SUPERCAPACITOR POROUS ELECTRODE

ELECTROLYTE SEPARATOR
DOUBLE LAYER ASSYMETRIC CAPACITOR

POLYPYRROLE ASSYMETRIC CAPACITOR

Li⁺

LMO

Cl⁻

Li⁺
PPY-LMO HYBRID ASSYMMETRIC LITHIUM ION CHLORIDE SELECTIVE SUPERCAPACITOR
Two-Step Process: LiCl capture and recovery
SIMULATION OF 2D BATTERY-REACTOR DURING LITHIUM INSERTION

3 $\times$ 10$^4$ m/s
50 A/ m$^2$
STABILITY OVER 200 CYCLES

ENERGY BALANCE

\[ W = \int \Delta E \cdot dq \]

10 Wh/mol lithium
(considering 50% efficiency)
Extraction from brine (insertion)  
Recovery of LiCl

\[ \frac{q_{\text{measured}}}{q_{\text{theory}}} \]

cycle number

- Extraction from brine (insertion)
- Recovery of LiCl
Conclusions

Li\textsubscript{1-x}Mn\textsubscript{2}O\textsubscript{4} (0 \leq x \leq 1) Li\textsuperscript{+} insertion electrode and Polypyrrole Cl\textsuperscript{-} 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\textsuperscript{+})
f. Overall cell voltage < 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\textsuperscript{+} is no co-inserted with Li\textsuperscript{+}.
j. Surface adsorption/occlusion of NaCl requires careful rinsing.
k. Adsorption model applies to the Li\textsuperscript{+} ion transfer at the Li\textsubscript{1-x}Mn\textsubscript{2}O\textsubscript{4} /brine interface.
l. Na\textsuperscript{+} adsorption at Li\textsubscript{1-x}Mn\textsubscript{2}O\textsubscript{4} blocks sites for Li\textsuperscript{+} adsorption
NEW LITHIUM RESEARCH CENTER IN JUJUY, ARGENTINA

Province of Jujuy, Argentina
CONICET
University of Jujuy
THANKS

https://www.sciencecananchangetheworld.org/