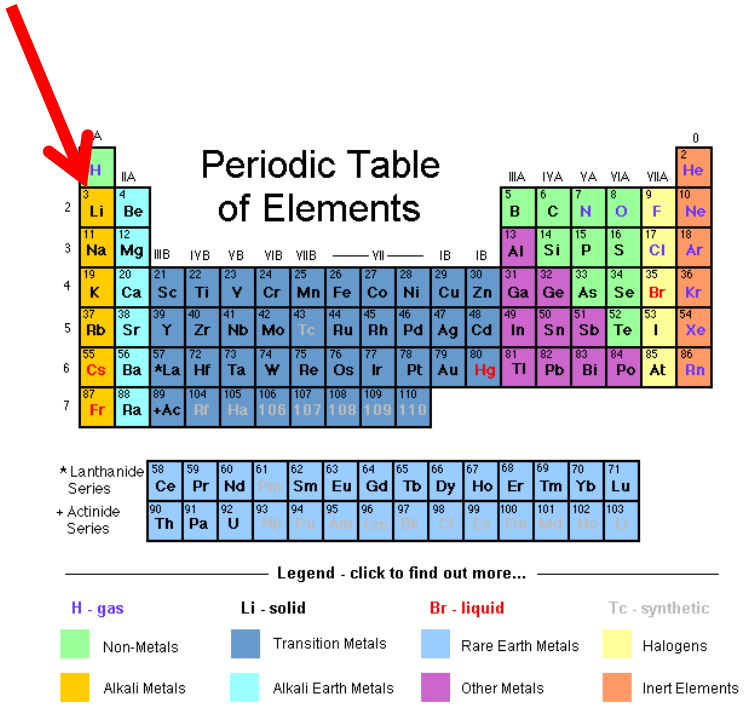
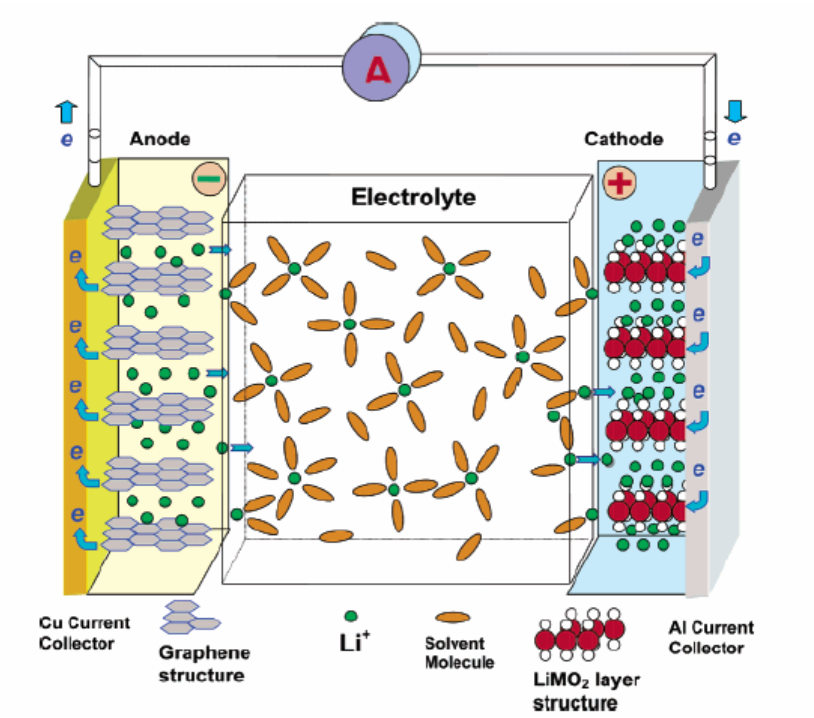
Baterías de Litio

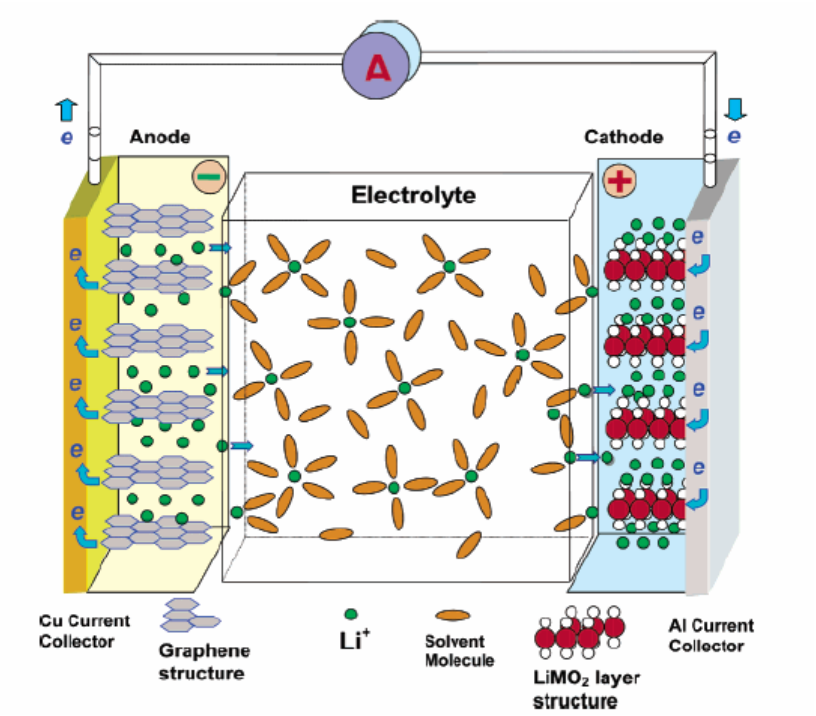
Porqué Li?

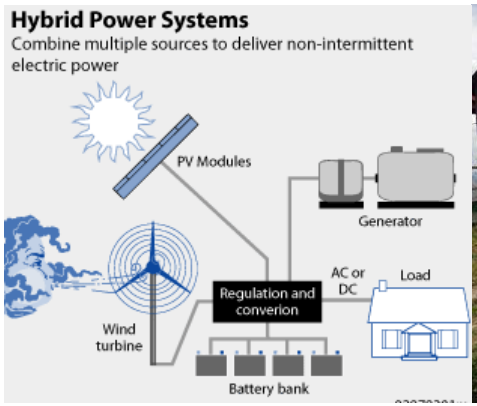

Periodic Table of Elements
Lanthanide Series
Actinide Series
Legend - click to find out more...
H - gas
Li - solid
Br - liquid
Tc - synthetic
Non-Metals
Transition Metals
Rare Earth Metals
Halogens
Alkali Metals
Alkali Earth Metals
Other Metals
Inert Elements


A
Anode
Cathode
Electrolyte
e
Cu Current Collector
Graphene structure
Li+
Solvent Molecule
LiMO2 layer structure
Al Current Collector

Porqué Li?

Li	
N.A.	3
P.A.	6,939
Densidad	0,53 g cm^{-3}
Capacidad	3,88 A.h/g
Potencial	-3,05 V vs. ENH

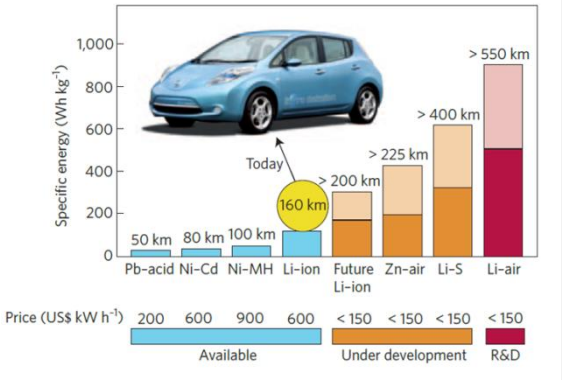




Remote Electrification (7.5 GWh market in South America)

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

We observe an accelerated move to low-carbon transport

Volkswagen announces that it will roll out 80 new electric cars across its multi-brand group by 2025, up from a previous goal of 30, and wants to offer an electric version of each of its 300 group models by 2030. (12 Sept 2017)

BMW plans 25 all-electric and hybrid vehicles by 2025. (7 Sept 2017)

Honda will offer an electrified version of all of its new models launched in Europe from now on. (12 Sept 2017)

Honda, Toyota and Shell have teamed up to introduce more hydrogen refueling stations in California. (13 Sept 2017)

Hyundai has announced plans to rapidly roll out new all-electric models as the giant Korean car maker looks to explore new tech in the pursuit of more stable profits. (18 Aug 2017)

Volvo has announced that every Volvo it launches from 2019 will have an electric motor, marking the historic end of cars that only have an internal combustion engine (ICE) and placing electrification at the core of its future business. (5 June 2017)

The governments of **France and the U.K.** will ban sales of diesel and gasoline fueled automobiles by 2040. (July 2017)

China has announced that it will require all car manufacturers to have EV sales of 12% of total sales by 2020, and is planning to ban the sale of internal combustion engine powered cars by date that is to be decided. (June 2017, Sept 2017)

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

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

GIGAFACTORY TESLA

Electric Avenue. Sparks, NV 89434, EEUU

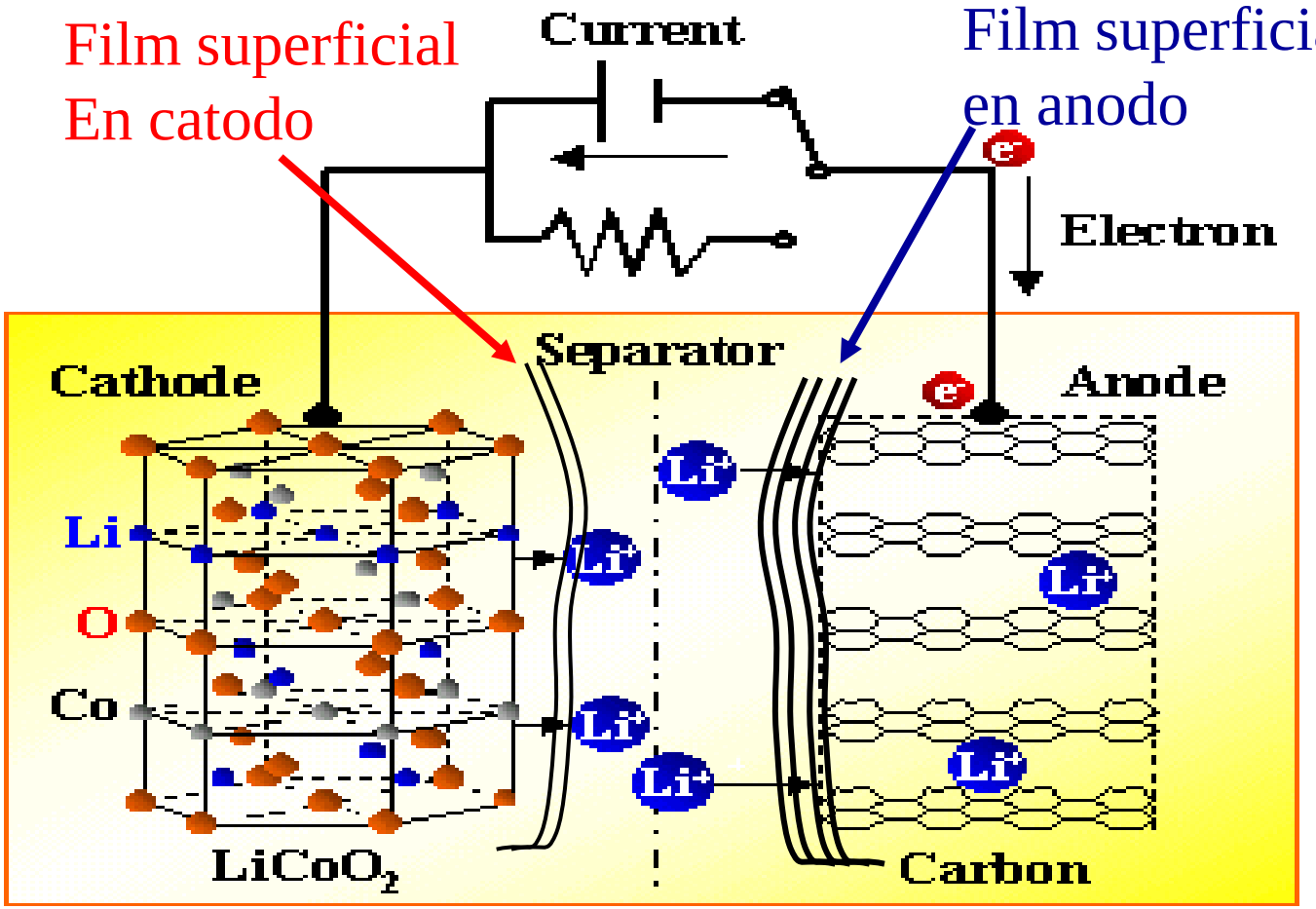
Tesla plans to manufacture 500.000 electric cars in 2018 (aprox. 2.250 ton of litium)

Baterias de Ion Litio

Las baterias de ion Li^+ ion usan varios componentes

Catodo

Li_XCoO_2



Anode

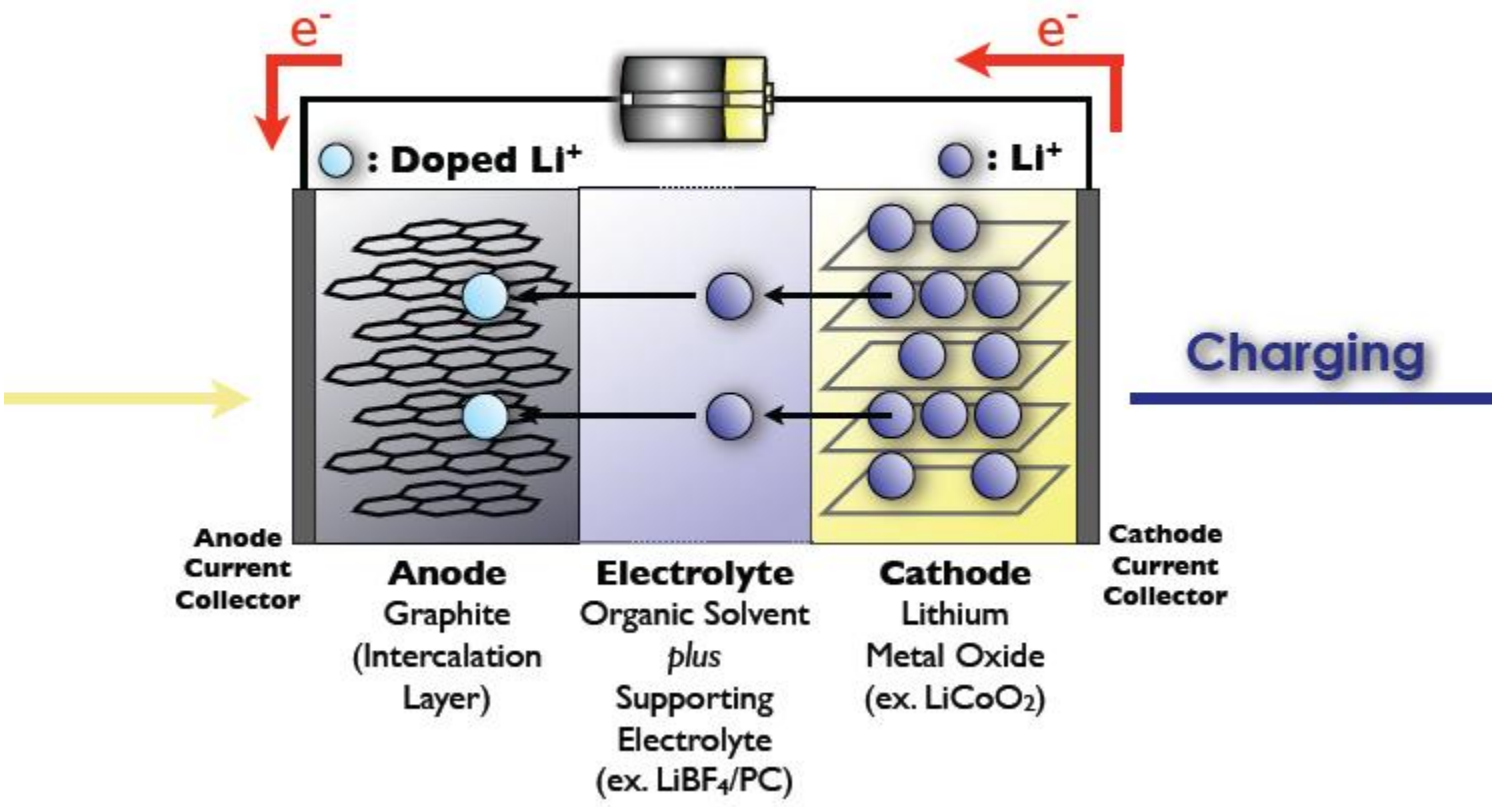
Li_XC_6

Soludion de Electrolito: Carbonato de Etileno & Di-Metil Carbonato/ $LiPF_6$

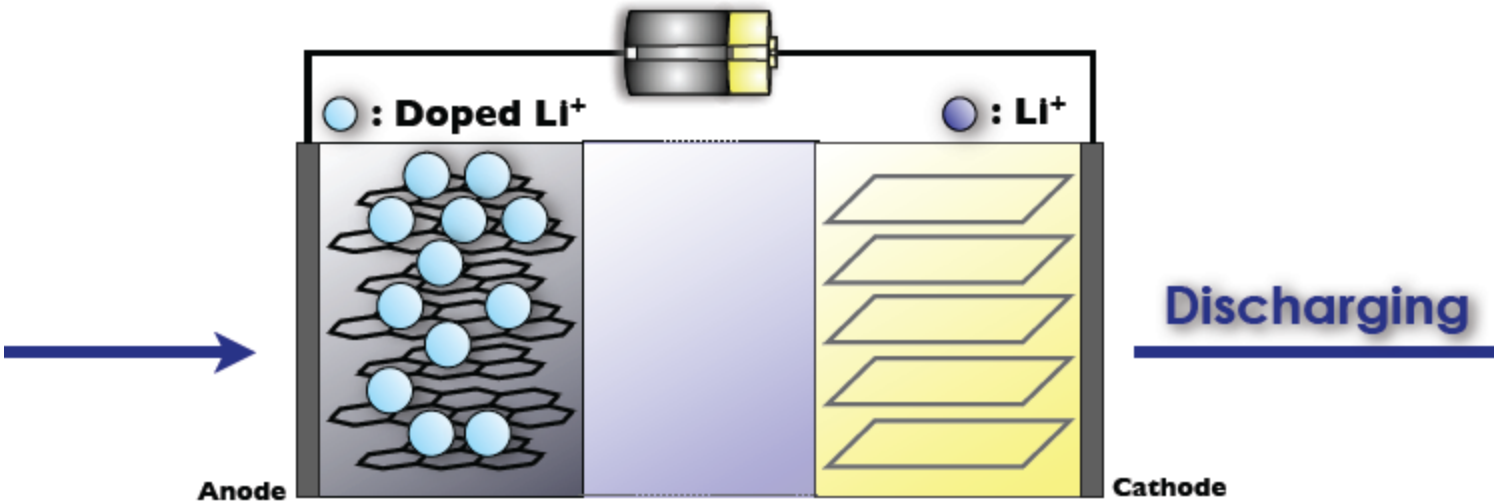
Voltage: 3.7 V, Densidad de Energia Media: 150 Wh/Kg

Mecanismo de Baterías de Li-ion

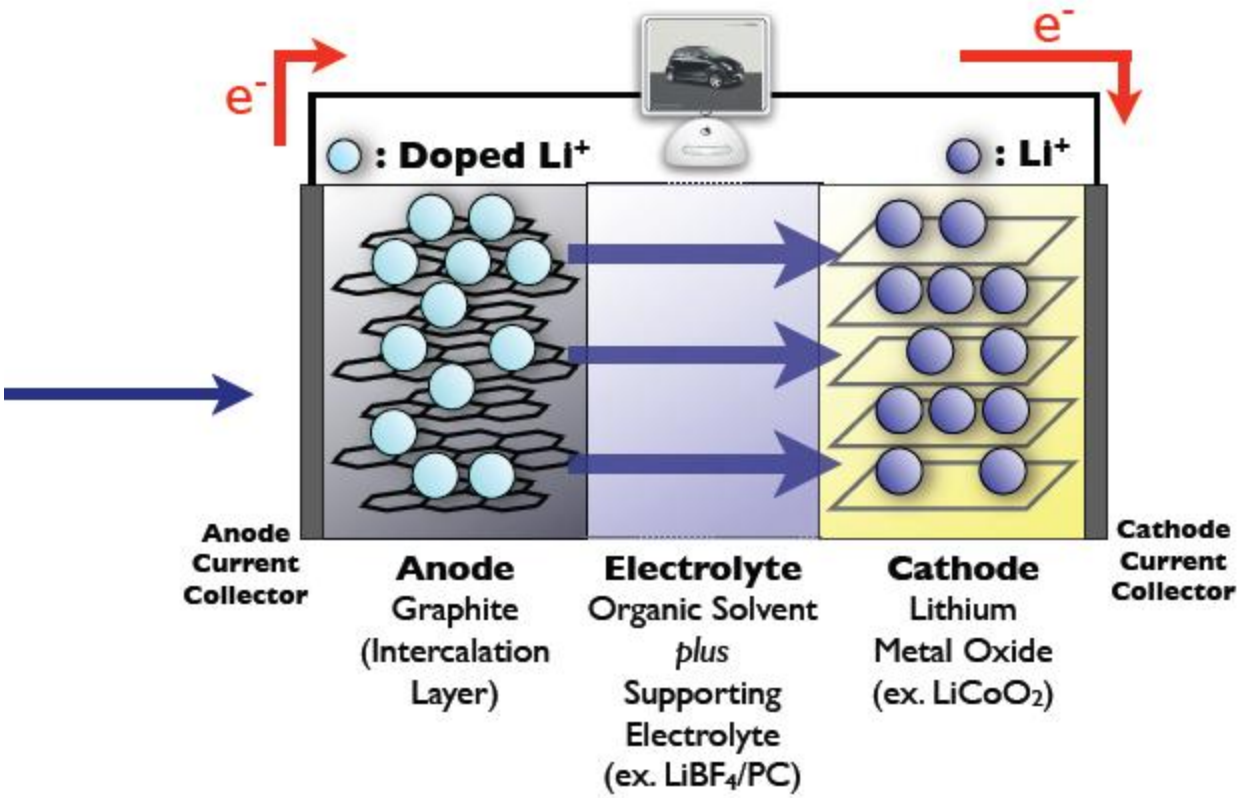
Sillón Hamaca (rocking chair)



Fully Charged State



Fully Discharged State

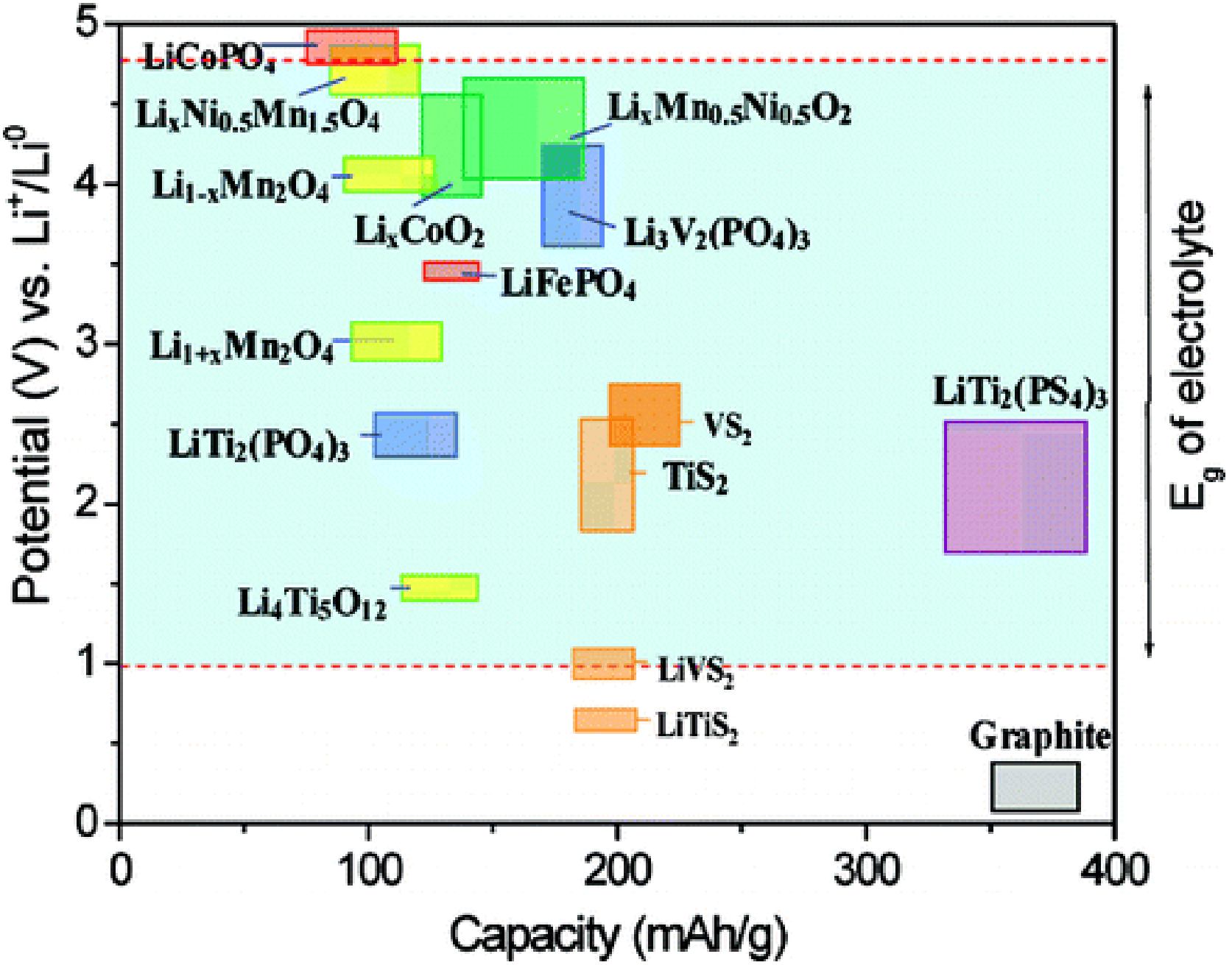


Anodo (-)

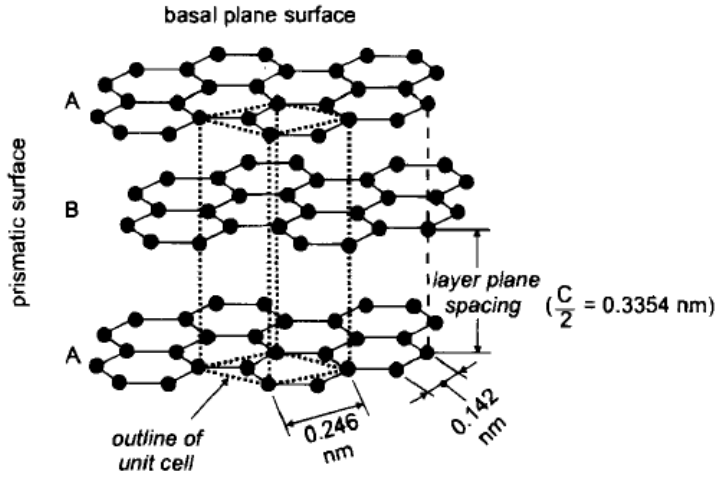
Electrode material	Average potential difference	Specific capacity	Specific energy
Graphite (LiC_6)	0.1-0.2 V	372 mA·h/g	0.0372-0.0744 kW·h/kg
Hard Carbon (LiC_6)	? V	? mA·h/g	? kW·h/kg
Titanate ($Li_4Ti_5O_{12}$)	1-2 V	160 mA·h/g	0.16-0.32 kW·h/kg
Si ($Li_{4.4}Si$)[28]	0.5-1 V	4212 mA·h/g	2.106-4.212 kW·h/kg
Ge ($Li_{4.4}Ge$)[29]	0.7-1.2 V	1624 mA·h/g	1.137-1.949 kW·h/kg

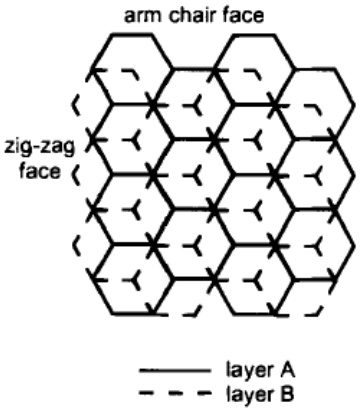
Catodo (+)

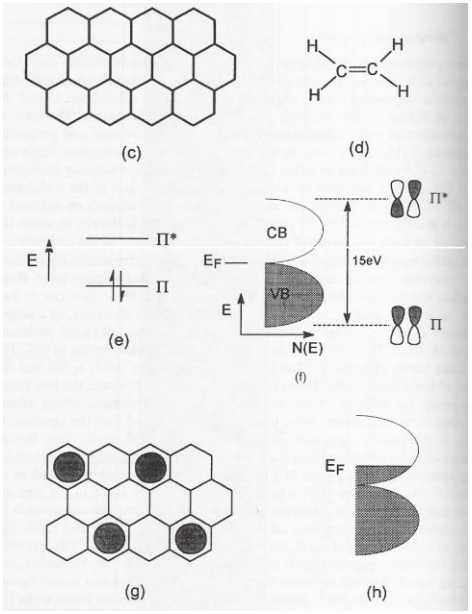
Electrode material	Average potential difference	Specific capacity	Specific energy
$LiCoO_2$	3.7 V	140 mA·h/g	0.518 kW·h/kg
$LiMn_2O_4$	4.0 V	100 mA·h/g	0.400 kW·h/kg
$LiNiO_2$	3.5 V	180 mA·h/g	0.630 kW·h/kg
$LiFePO_4$	3.3 V	150 mA·h/g	0.495 kW·h/kg
Li_2FePO_4F	3.6 V	115 mA·h/g	0.414 kW·h/kg
$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	3.6 V	160 mA·h/g	0.576 kW·h/kg
$Li(Li_aNi_xMn_yCo_z)O_2$	4.2 V	220 mA·h/g	0.920 kW·h/kg

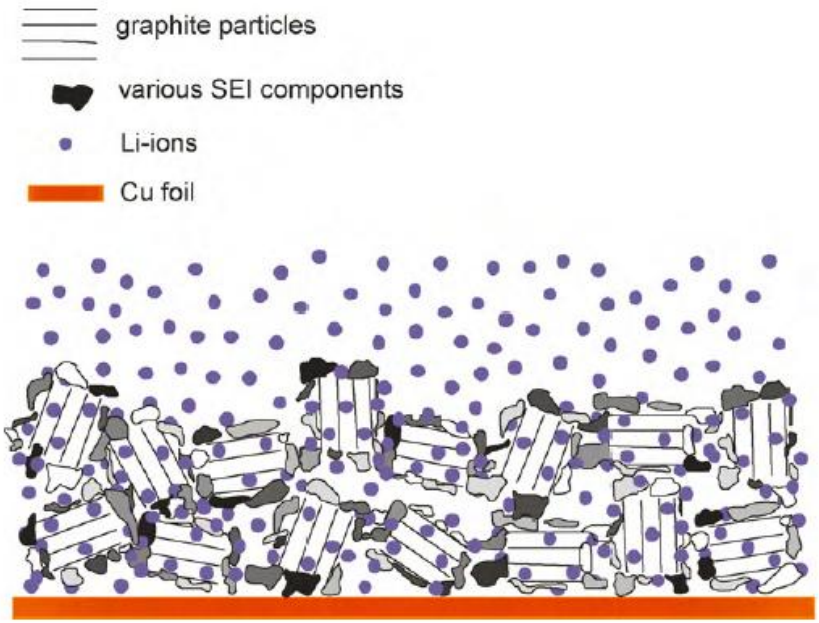

Potential (V) vs. Li+/Li0
Capacity (mAh/g)
Eg of electrolyte
LiCoPO4
LixNi0.5Mn1.5O4
LixMn0.5Ni0.5O2
Li1-xMn2O4
LixCoO2
Li3V2(PO4)3
LiFePO4
Li1+xMn2O4
LiTi2(PS4)3
LiTi2(PO4)3
VS2
TiS2
Li4Ti5O12
LiVS2
LiTiS2
Graphite
0
1
2
3
4
5
0
100
200
300
400

Ánodo de Grafito









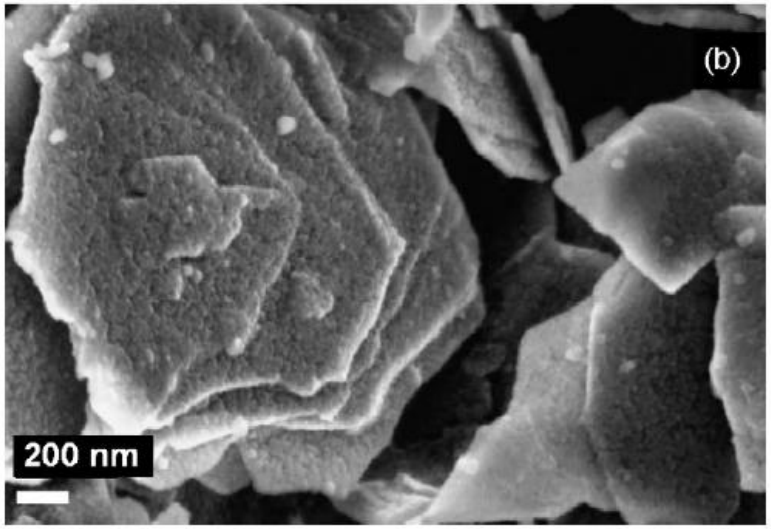
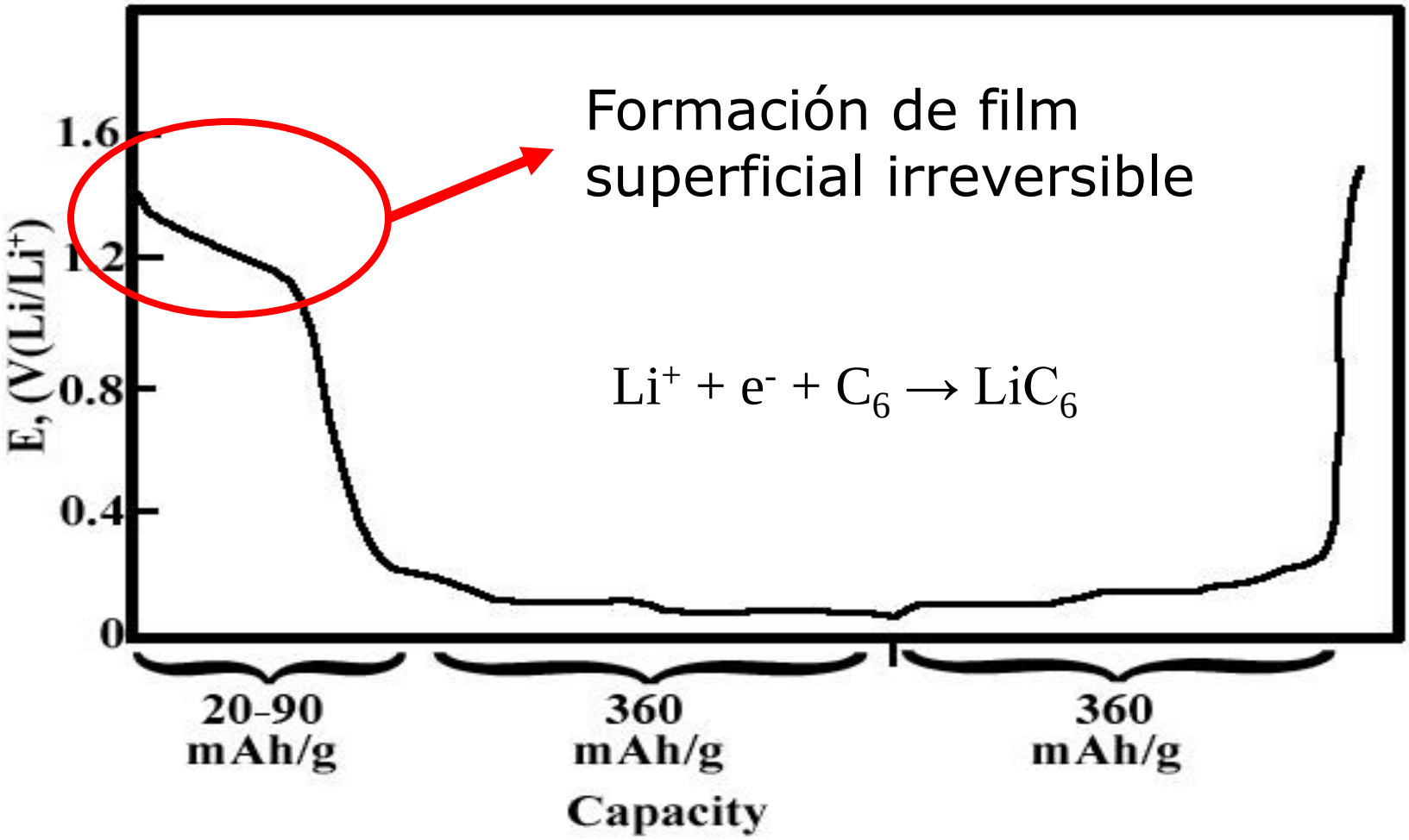


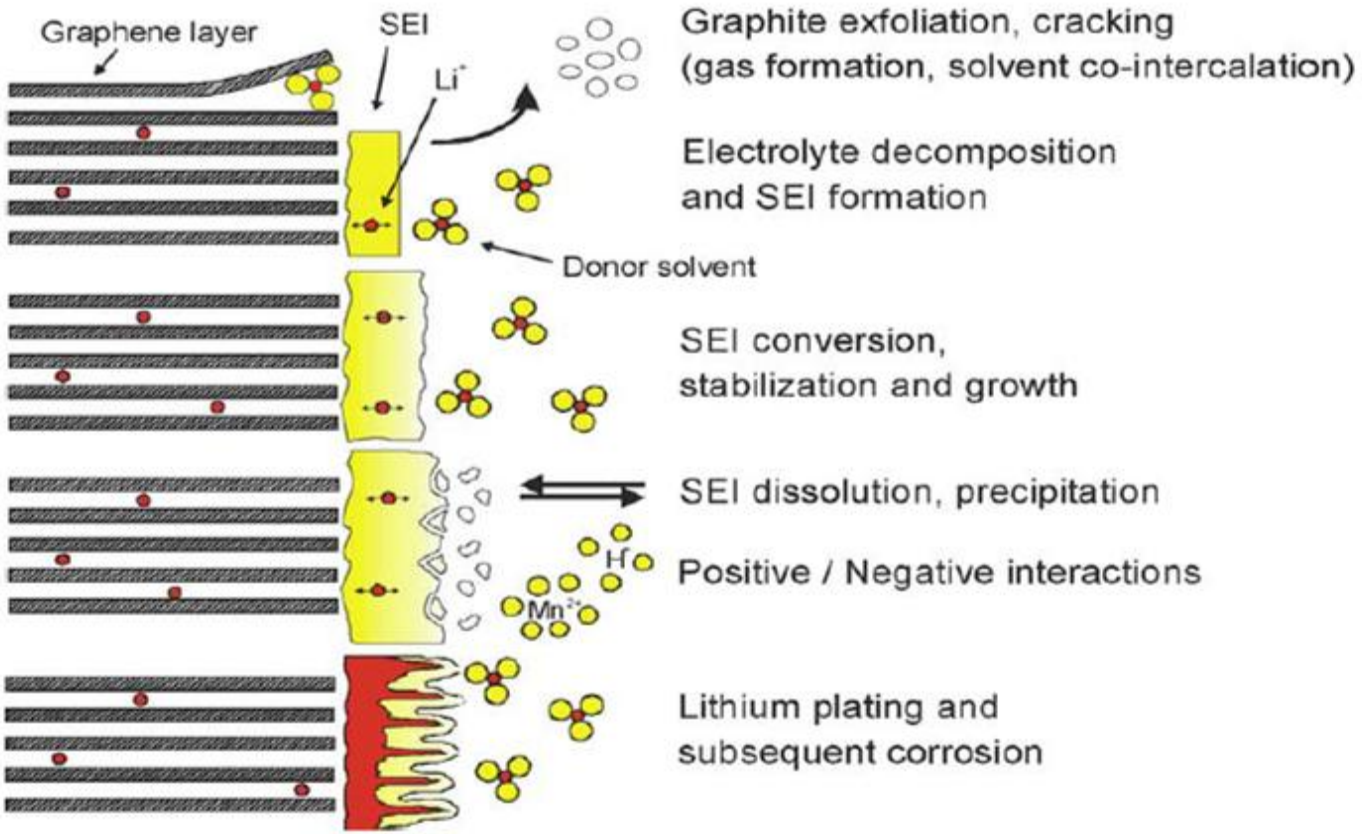
Fig. 3. SEM of composite SFG6 (TIMCAL®) graphite electrode (90% graphite and 10% PVDF-HFP binder): (a) pristine electrode and (b) electrode after one cycle vs. Li metal in 1 M $LiPF_6$ in EC:DMC (1:1) electrolyte at C/10 rate.

Perfil de Potencial

Primer Ciclo



Formacion de un film superficial, SEI



Changes at the anode/electrolyte interface, from *J. Vetter et al. / Journal of Power Sources 147 (2005) 269–281*

Cátodo de Inserción de ión Li^+

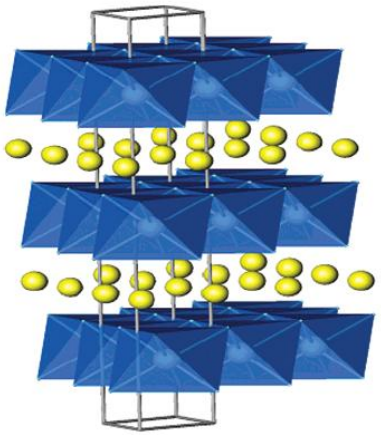


Figure 1. Layered structure of $LiTiS_2$, $LiVSe_2$, $LiCoO_2$, $LiNiO_2$, and $LiNi_yMn_yCo_{1-2y}O_2$, showing the lithium ions between the transition-metal oxide/sulfide sheets. The actual stacking of the metal oxide sheets depends on the transition metal and the anion.

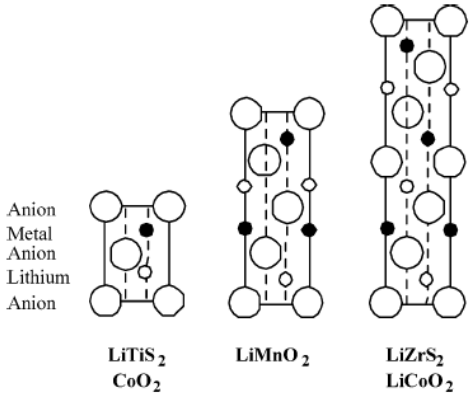
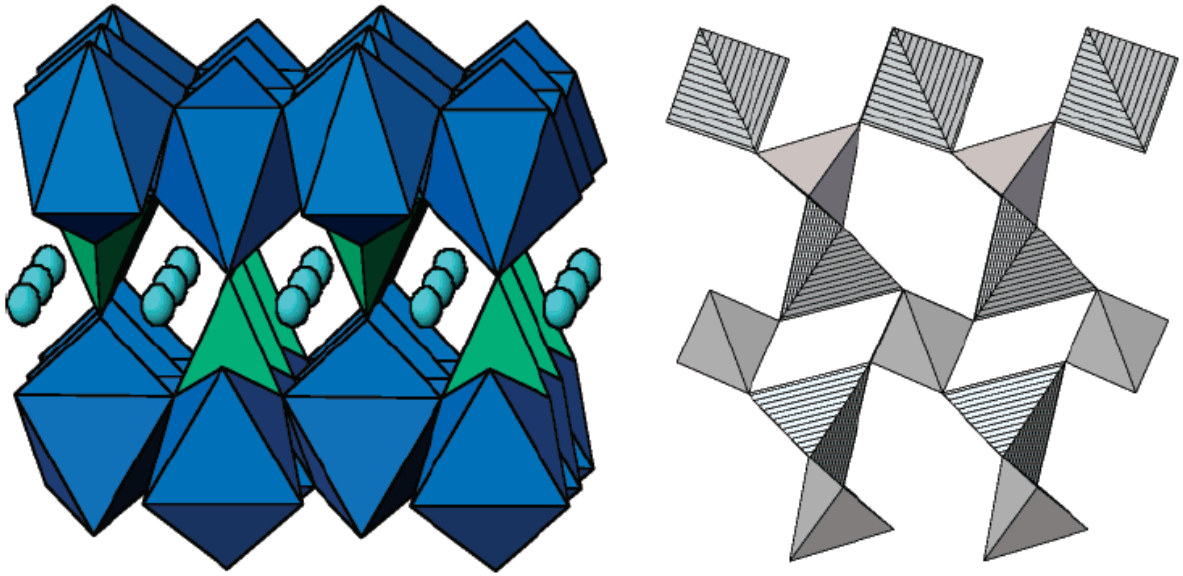


Figure 10. Schematic of stacking of building blocks for one-block, two-block, and three-block structures.



Structures of orthorhombic $LiFePO_4$ and trigonal quartz-like $FePO_4$.

Separadores

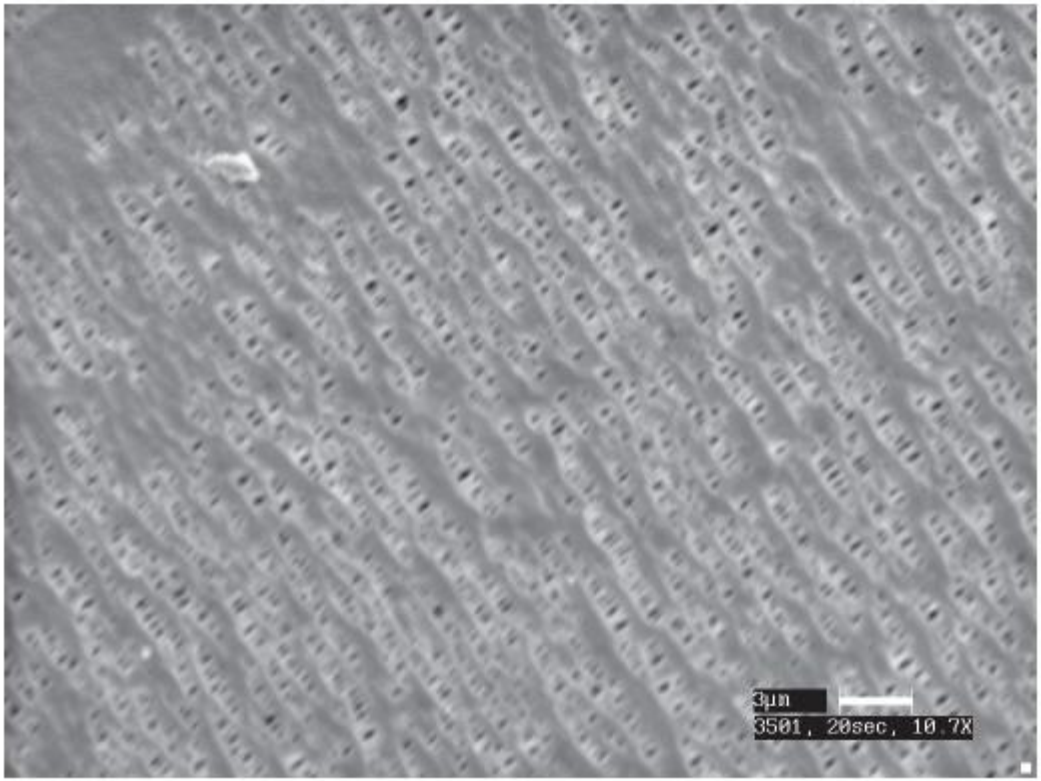


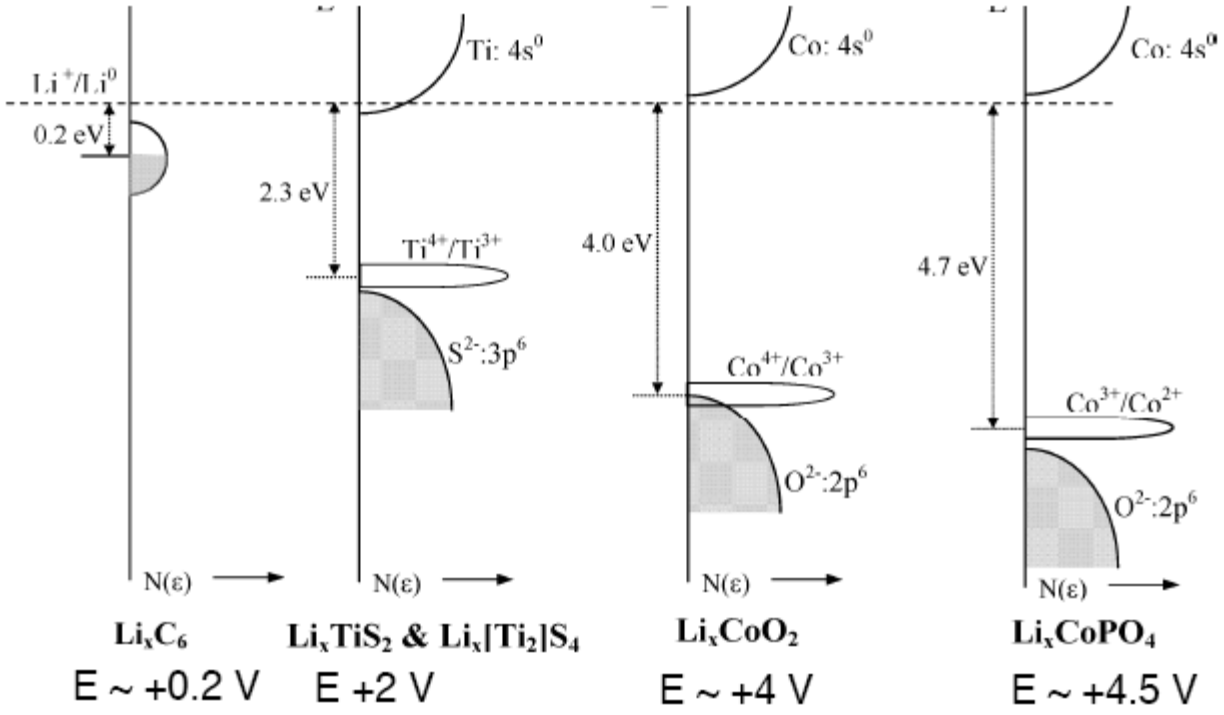
FIGURE 35.28 SEM micrograph of Celgard 3501 separator. (*Courtesy of Yardney Technical Products, Inc.*)

What determines the electrode potential?

$E = -\mu_{Li}/F = -(\mu_{Li+} + \mu_e)/F$

1. The ELECTRON ENERGY

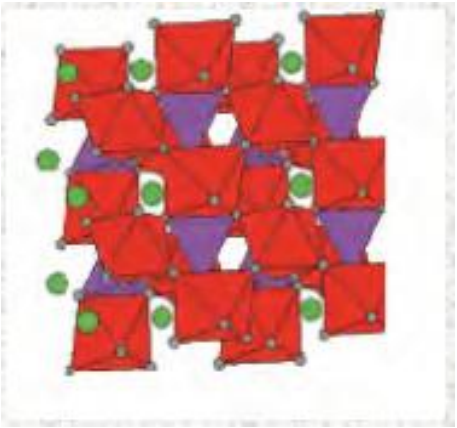
The Fermi level is the chemical potential of the electron, μ_e (always –ve

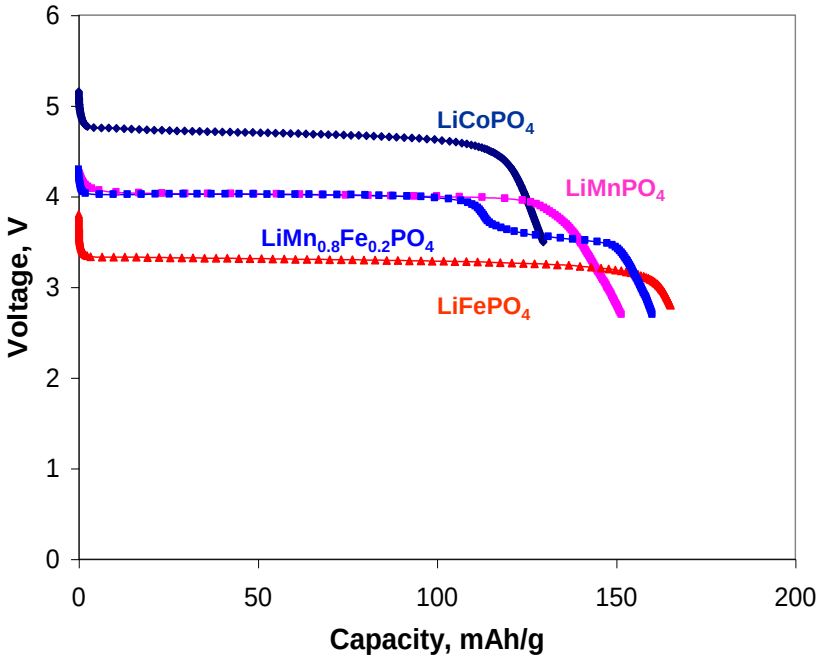


Goodenough and Kim, Chem. Mater., 22, (2010), 587-603

The $LiMPO_4$ Family: Optimization of Olivine Cathodes for Li-ion Batteries

Olivine	Voltage Range (V)	theoretical Energy Density (mAh/ g)
$LiFePO_4$	3.4	170 (165 practical)
$LiMnPO_4$	4.2	170 (150 practical)
$LiMn_{0.8}Fe_{0.2}PO_4$	4.2	170 (160 practical)
$LiCoPO_4$	4.8	170 (130-140 practical)





Advantages of olivine cathodes:

- High capacity
- Flat voltage profile

For $LiFePO_4$, $LiMnPO_4$, $LiMn_{0.8}Fe_{0.2}PO_4$:

- Low cost
- Low toxicity
- High rate capability

For $LiCoPO_4$

- High voltage

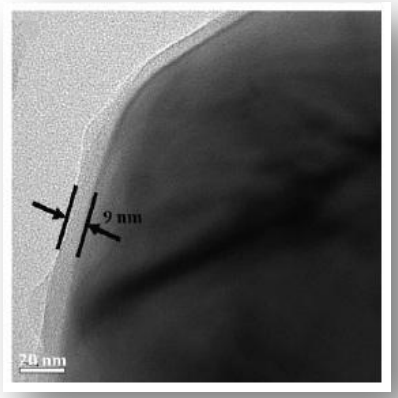
How to improve performance:

Electronic conductivity:

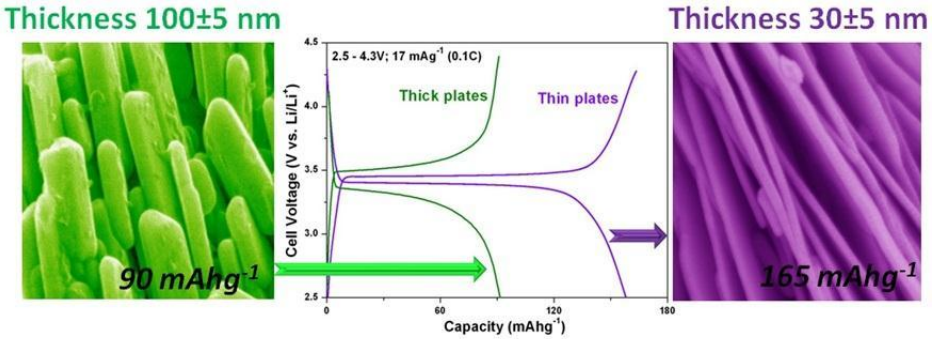
- Thin carbon coating
- Aliovalent dopants

Li-Ion Diffusion:

- Reduce particle size (nano particles)
- Aliovalent dopants
- Solid solution

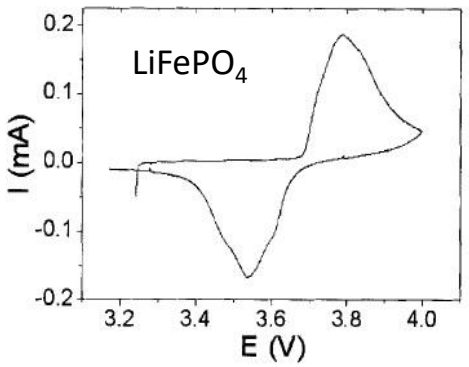


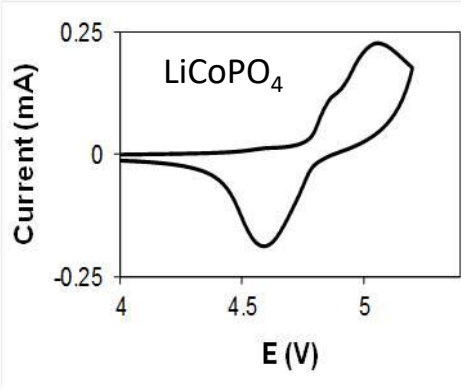
* HR-TEM image of the LiFe0.9Mg0.1 PO4/C sample

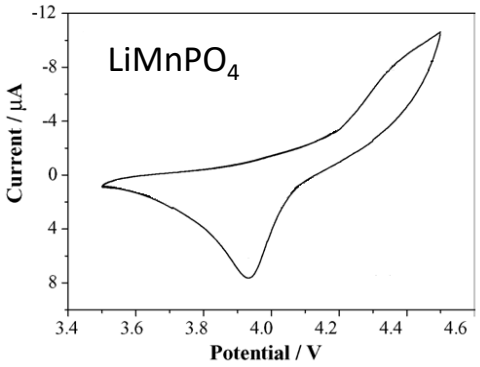


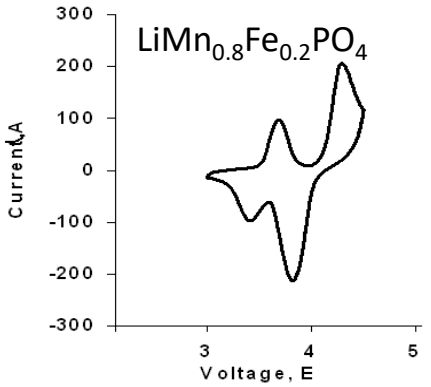
Comparison of $LiFePO_4$ nanoplates with thick plates [Saravanan et al. *J. Mater. Chem.*, 19 (2009) 605].

Cyclic voltammetry





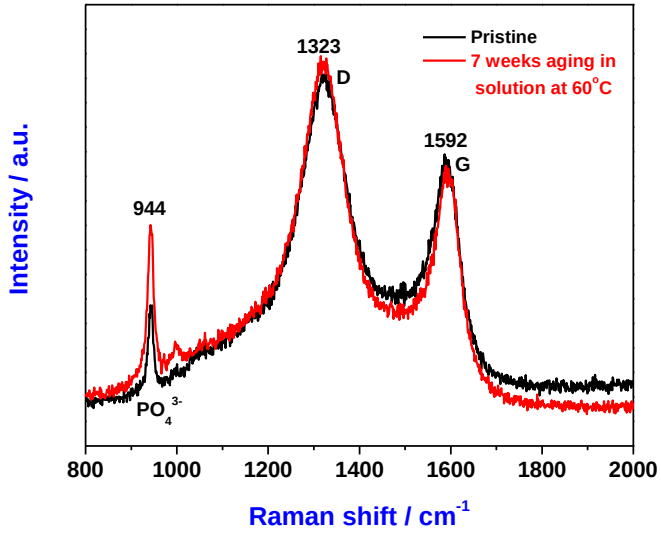




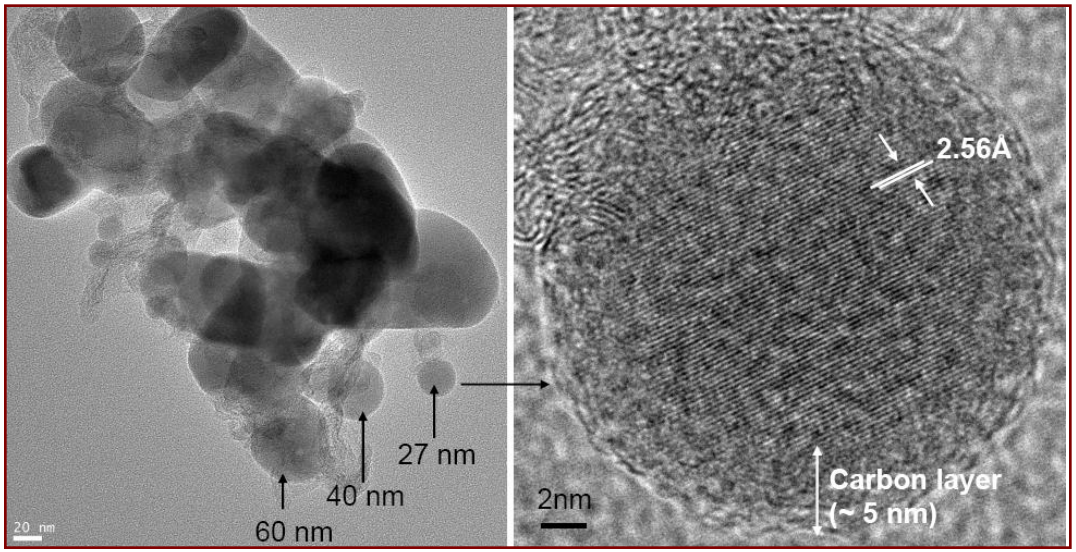
*** Hui Liua, Jingying Xie, *Journal of materials processing technology* , 209(2009) 477–481.**

Impact of Aging in Solutions: Morphology of C-$LiMn_{0.8}Fe_{0.2}PO_4$: Highly Stable

Raman

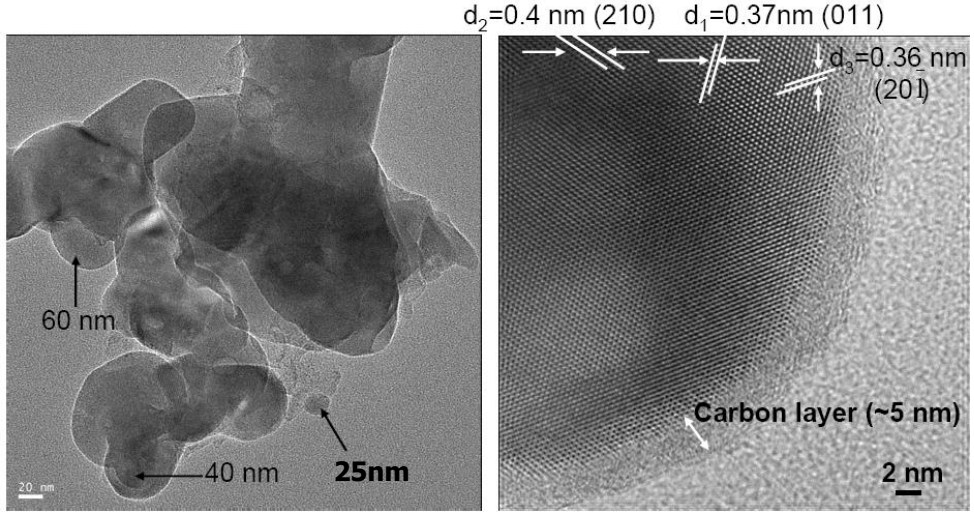


Pristine C-$LiMn_{0.8}Fe_{0.2}PO_4$



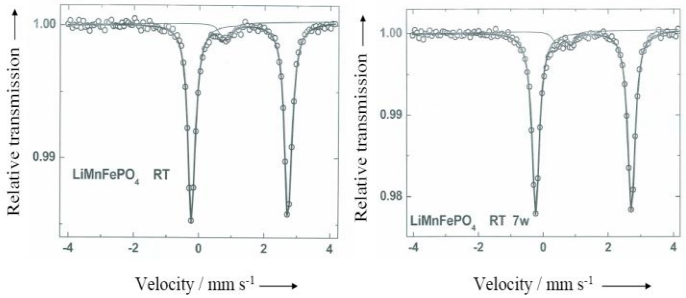
C-$LiMn_{0.8}Fe_{0.2}PO_4$ particles do not undergo any morphological changes upon prolonged aging at 60°C

3 week aged at 60°C



Mossbauer (Fe)

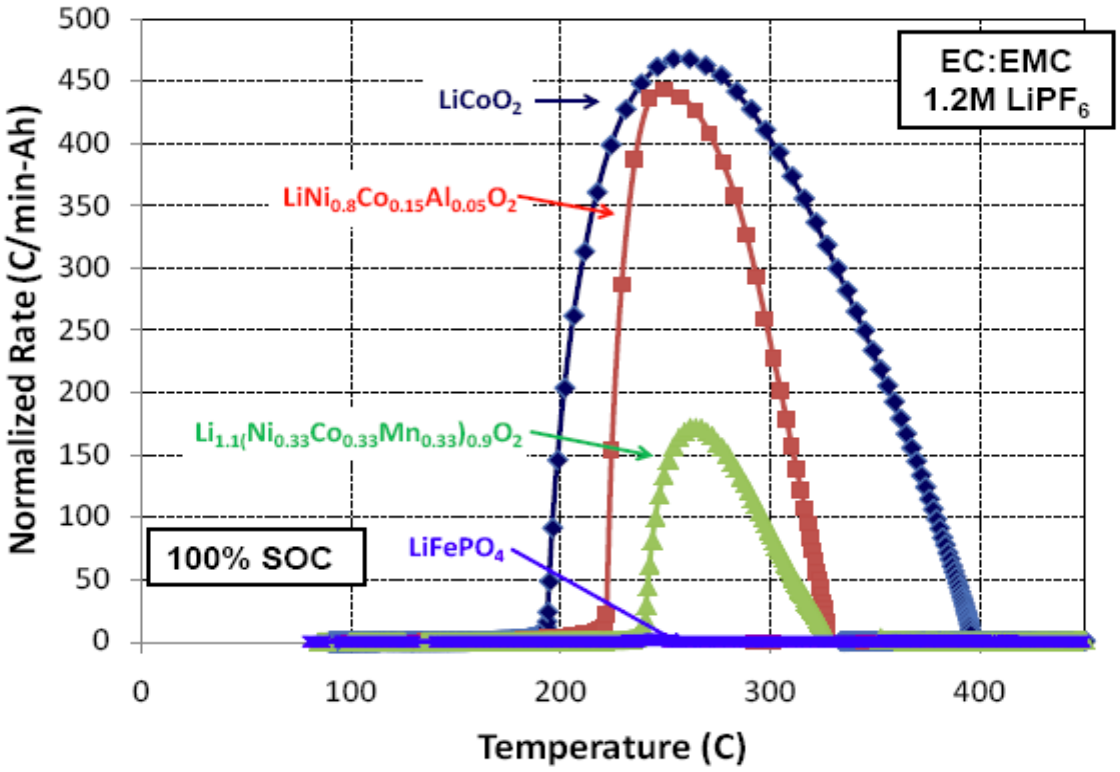
pristine



aged

Thermal Runaway & Cathode Chemistry

Accelerating Rate Calorimetry (ARC)



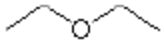
- *Increased thermal runaway temperature and reduced peak heating rate for full cells*
- *Decreased cathode reactions associated with decreasing oxygen release*

Published by Sandia National Laboratory (USA)

Electrolyte solutions for Li batteries

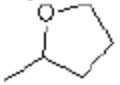
Solvents

Ethers

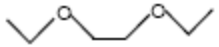


Diethyl ether (DEE)

Tetrahydrofuran (THF)



2-Methyltetrahydrofuran (2Me-THF)

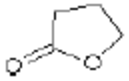


Diethoxyethane

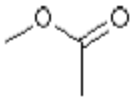
1,3-Dioxolane

Esters

Methyl formate (MF)

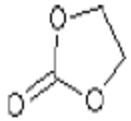


gamma-Butyrolactone (BL)

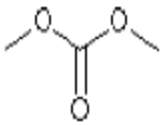


Methyl acetate

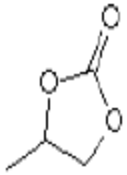
Alkyl carbonates



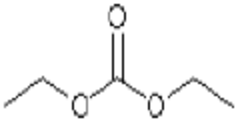
Ethylene carbonate (EC)



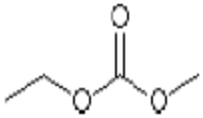
Dimethyl carbonate (DMC)



Propylene carbonate (PC)

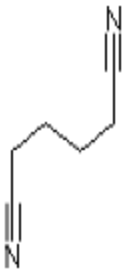


Diethyl carbonate (DEC)

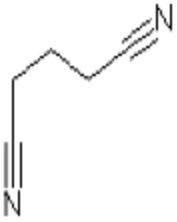


Ethyl methyl carbonate (EMC)

Nitriles

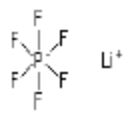


Adiponitrile (AN)

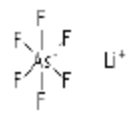


Glutaronitrile (AN)

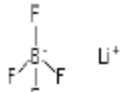
Relevant Li Salts



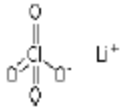
$LiPF_6$
Lithium hexafluorophosphate



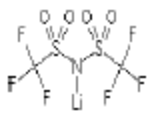
$LiAsF_6$
Lithium hexafluoroarsenate



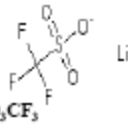
$LiBF_4$
Lithium tetrafluoroborate



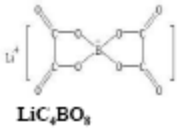
$LiClO_4$
Lithium perchlorate



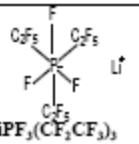
$LiN(SO_2CF_3)_2$
Lithium bis(trifluoromethane sulfonimide) (**LiTFSI**)



$LiSO_3CF_3$
Lithium trifluoromethane sulfonate (Lithium triflate)



LiC_4BO_8
Lithium bis(oxalate) borate (**LiBOB**)



$LiPF_3(CF_2CF_3)_3$
Lithium fluoroalkyl phosphate (**LiFAP**)

Baterias de litio-polímero

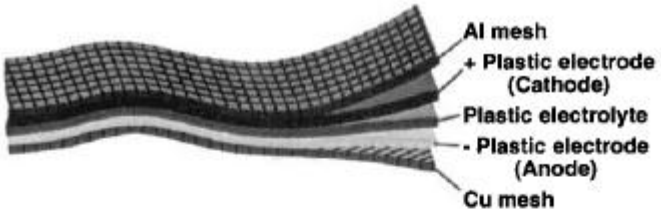


FIGURE 35.87 Schematic diagram showing the construction of a polymer Li-ion cell. (*Courtesy of Telecordia.*)

FIGURE 35.88 A 0.57 Ah polymer Li-ion battery. (*Courtesy of Sanyo.*)

DIFICULTADES

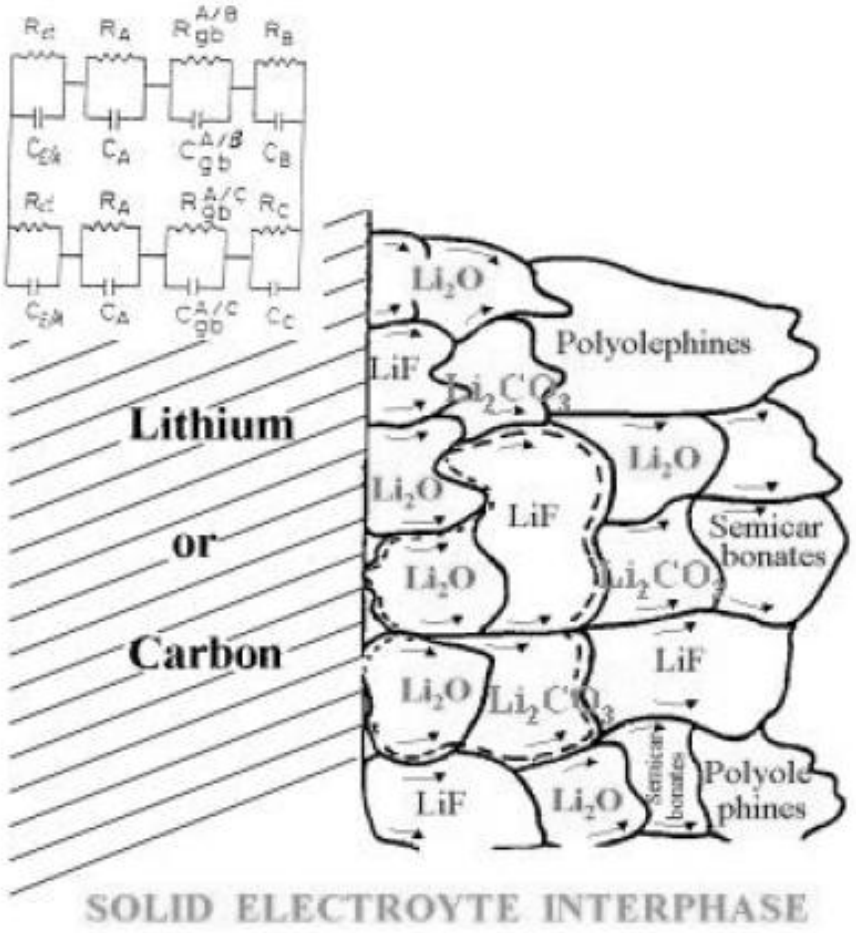
Las baterias son dispositivos muy complejos: 3 solidos activos (anodo, catodo, electrolito) y dos interfaces electrodo-electrolito deben fucionar simultanemente sin reacciones secundarias.

- **En baterias ion litio no hay estabilidad termodinamica**
- **En el anodo, por debajo de 1 V vs. Li/Li+ la mayoria de los solventes, aniones de las sales pueden reducirse en particular en presencia de iones Li+.**

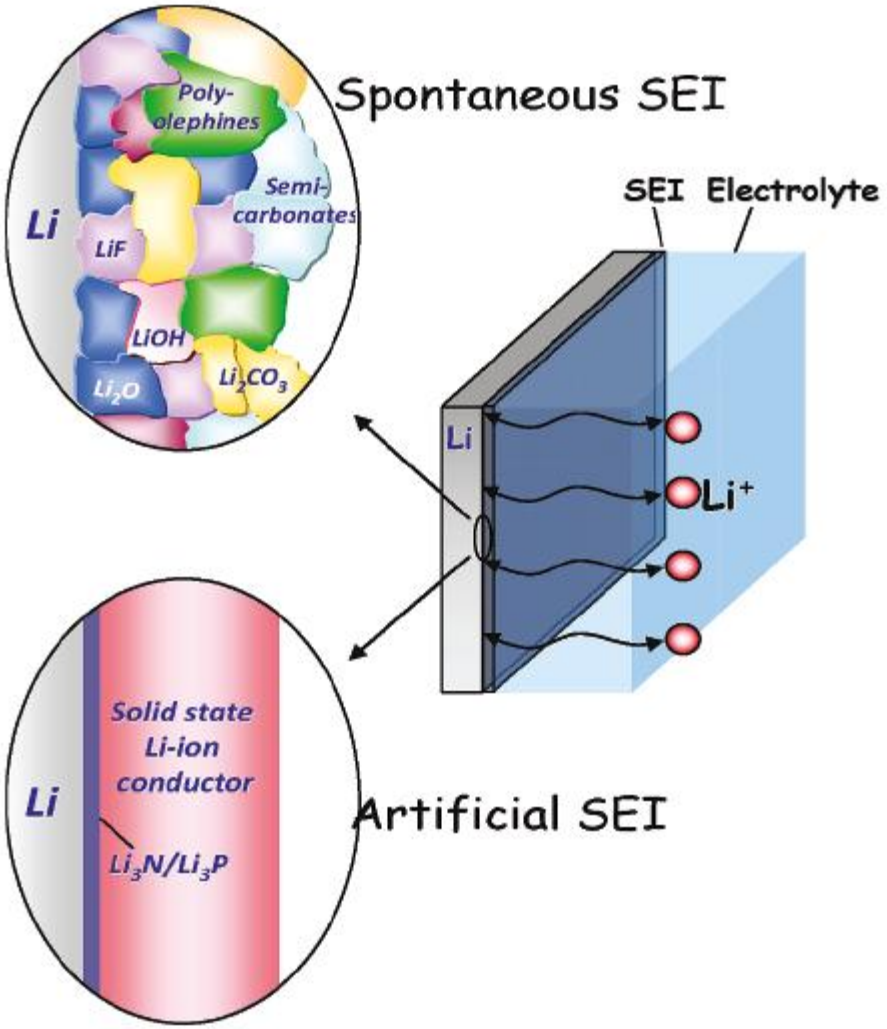
*** En el catodo: Todos los oxidos de metales de transicion litiados son nucelo-filicos y basicos, pueden reaccionar con solventes electrofilicos.**
Ocurren reacciones acido-base con HF y PF5, intercambio de protones con iones metalicos y disolucion.

- **En los catodos de-litiados podemos encontrar inestabilidad andica de solvente y problemas con colectores de corriente.**
- **Que colector de corriente usamos? La mayoria de los metales se disuelve a potenciales anodicos moderados. Los metales preciosos como Au y Pt son caros y cataliticos.**
- **Se eligio Al debido a su pasivacion, pero la pasivacion de Al no es estable mas alla de ciertos umbrales de potencial entre 4-5 V**

SOLID ELECTROLYTE INTERPHASE (SEI)

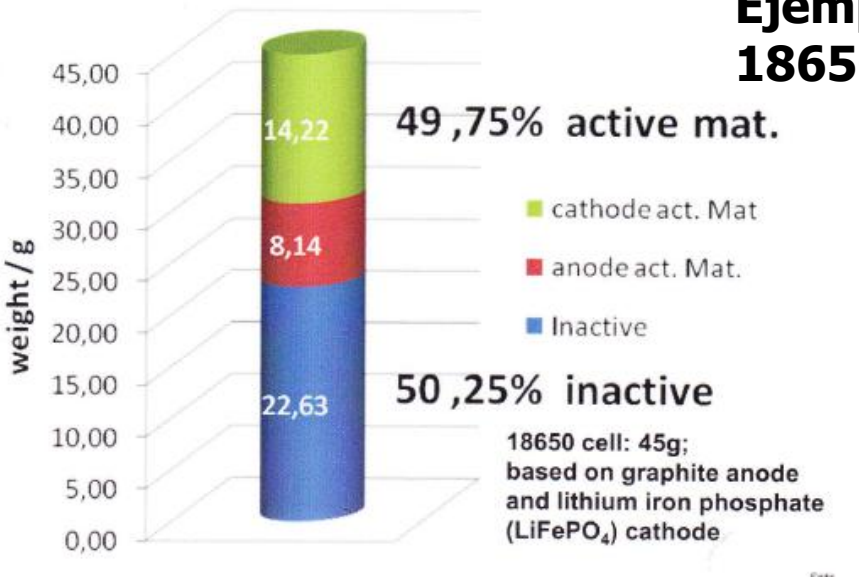


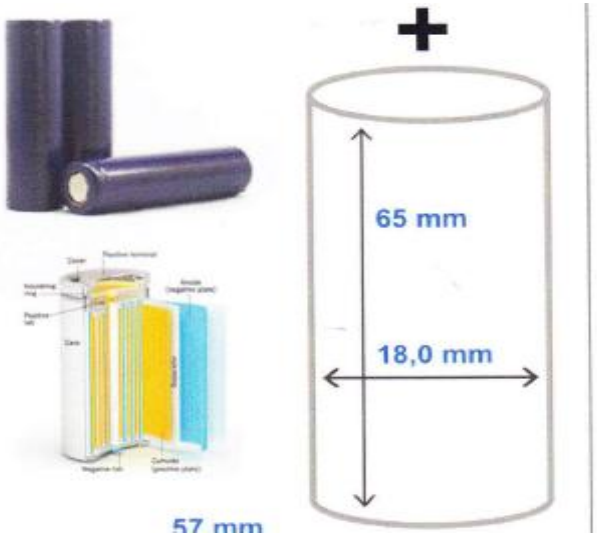
Interfaz Electrolito Solido (SEI)

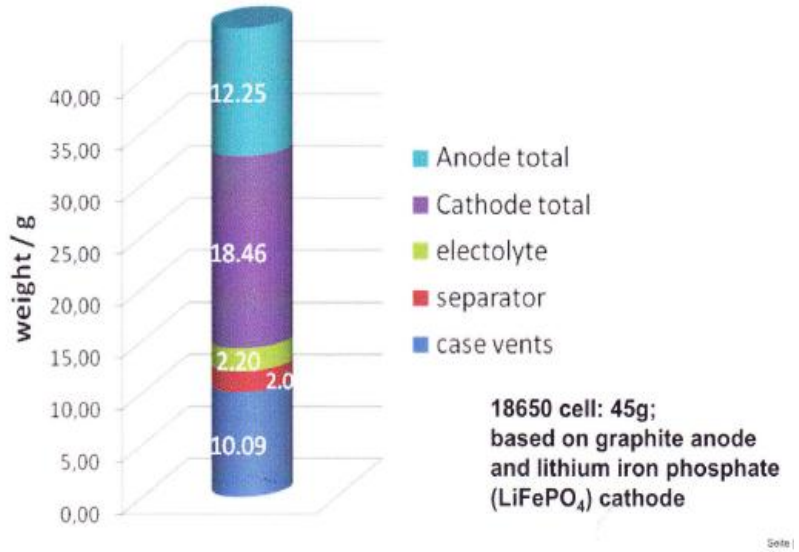


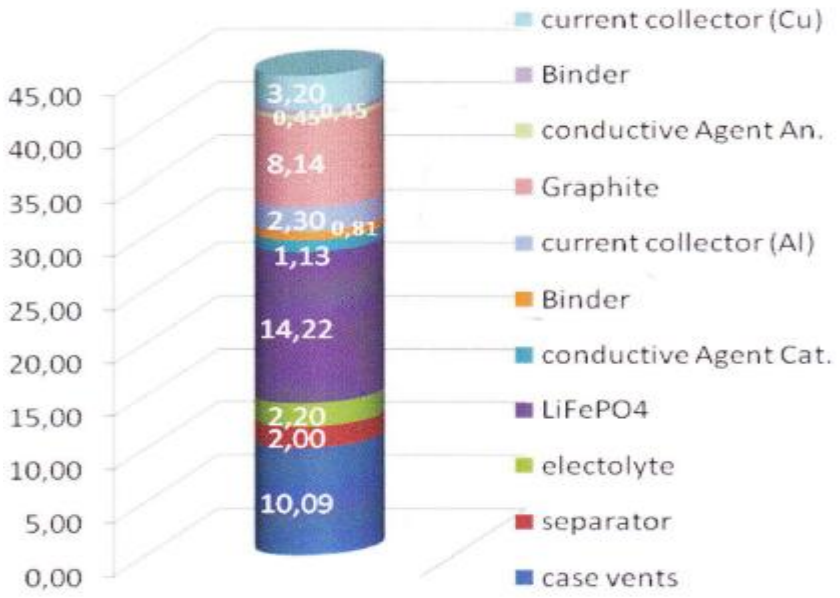
Baterias de ion litio comunes y su distribucion de masa

Ejemplo: 18650 celdas









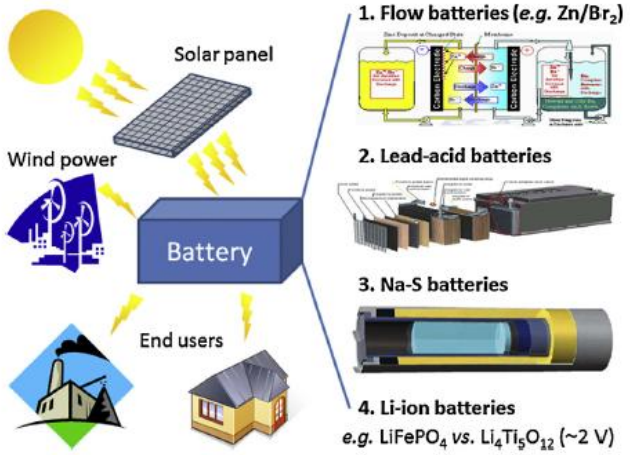
LITHUM BATTERY FOR SUSTAINABLE ENERGY STORAGE

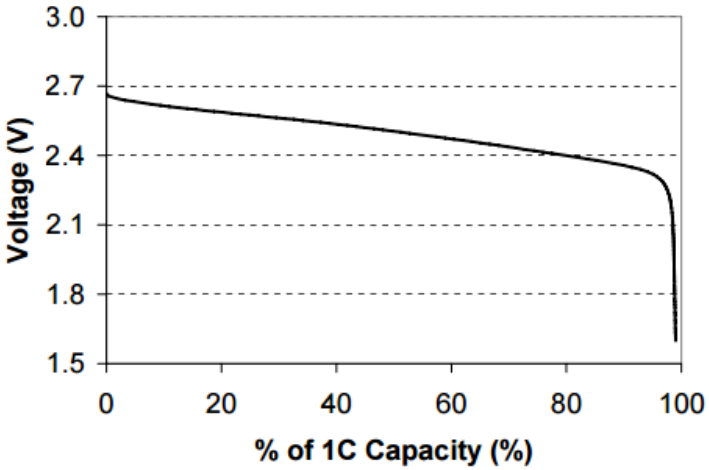
Positive Active Material (LMO):

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

Negative Active Material (LTO):

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





1C discharge
30ºC

E_{cell} = 2.5 V

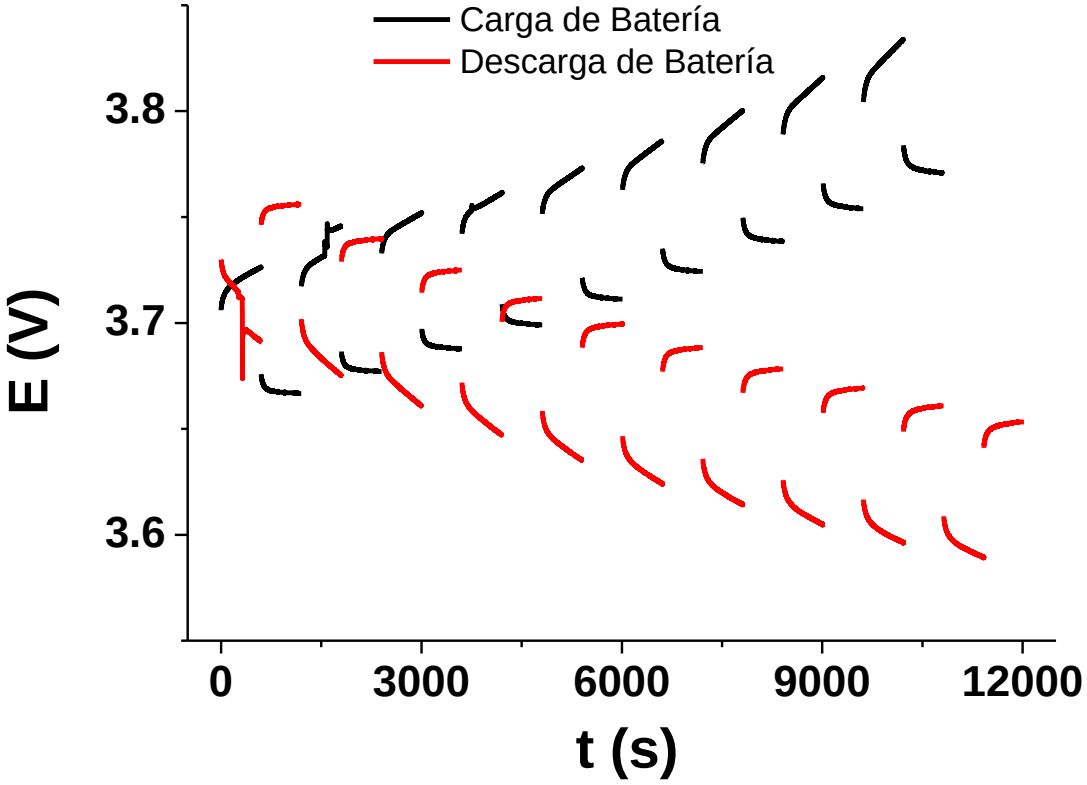
20.000 ciclos de carga y descarga
Vida útil de paneles solares, mas 20 años.

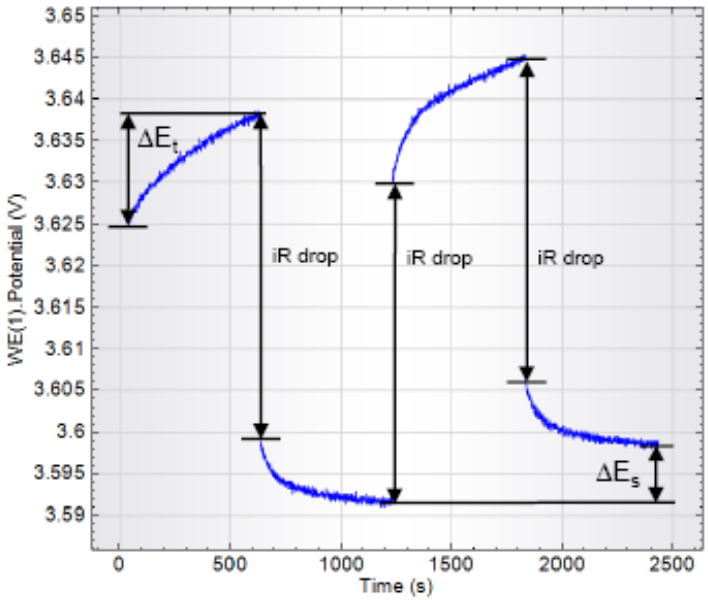
LTO/LMO battery
Much higher available energy and voltage than Ni-MHO

- **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.

Aplicación de Tecnica GITT a una bateria 18650 de Li ion de 2,4 Ah descargando a C/10 o sea con pulsos de corriente de 240 mA

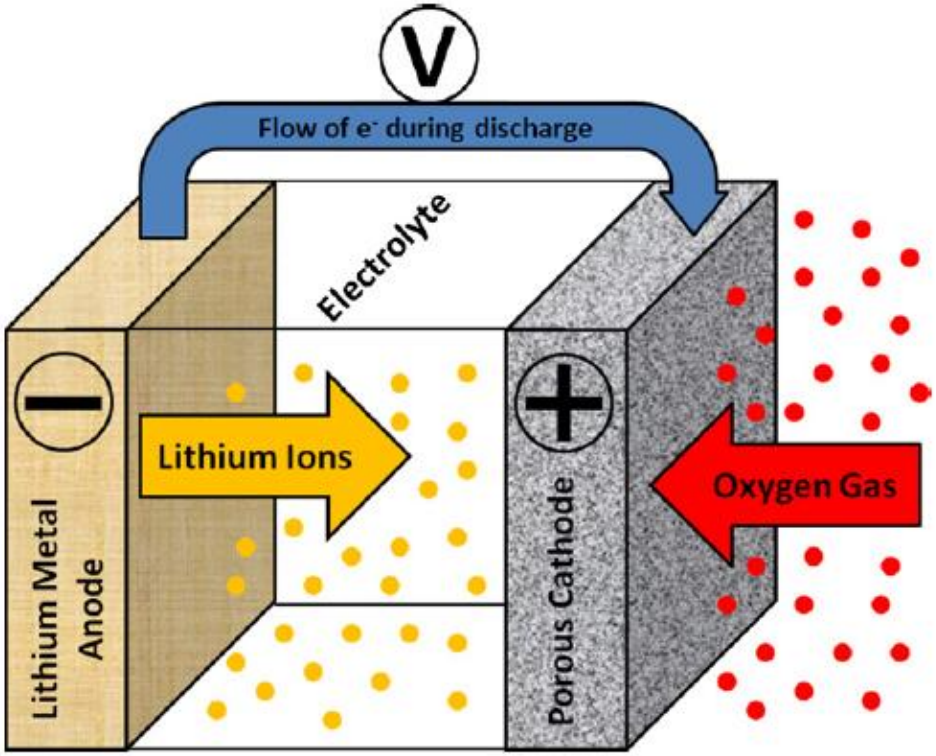


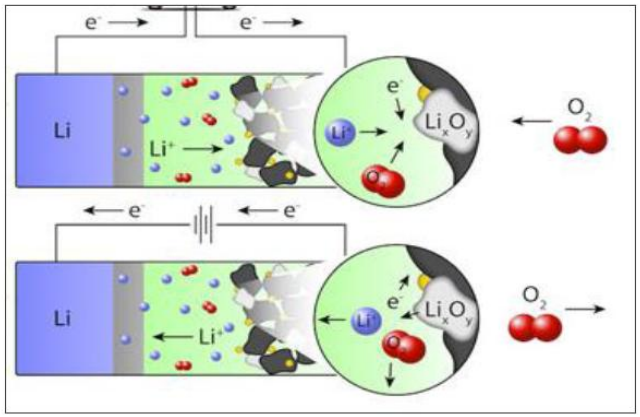


$$D = \frac{4}{\pi}\left(\frac{iV_m}{z_A FS}\right)^2 \left[\left(dE/d\delta\right) \Big/ \left(dE/d\sqrt{t}\right)\right]^2$$

$$D = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$

Rechargeable Li Air Batery





$$2Li + O_2 \rightarrow Li_2O_2$$

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

Lithium Anode

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

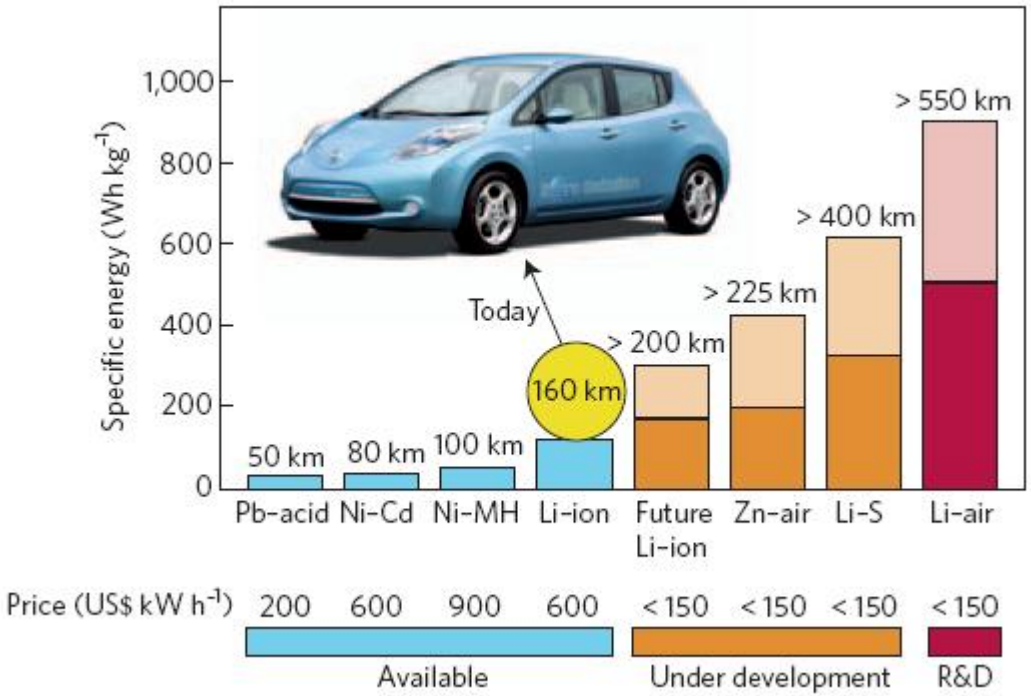
Carbon Cathode

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

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

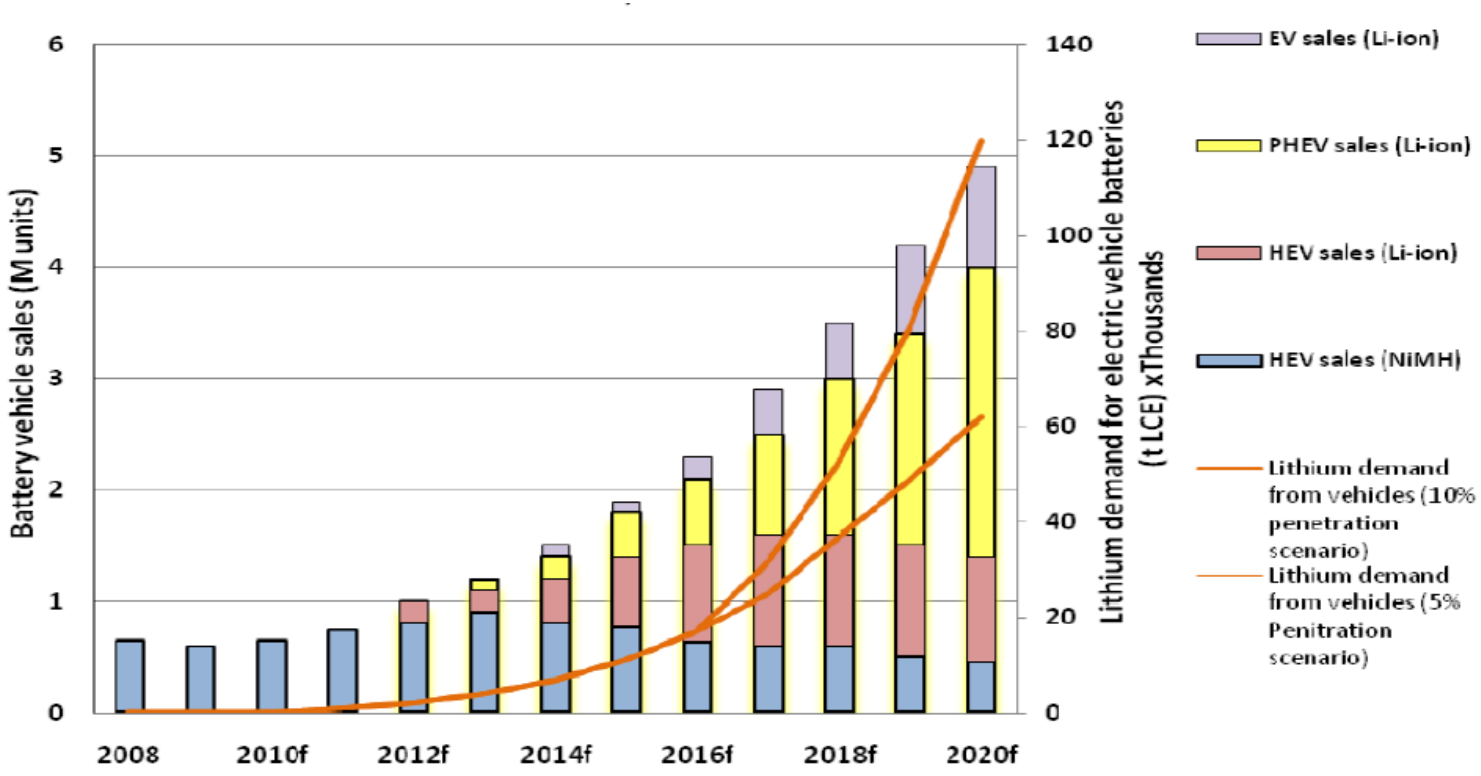
$$Li_2O_2 + 2(Li^+ + e^-) \rightarrow 2Li_2O \qquad U_0 = 2.72\ V$$

K.M. Abraham, Z. Jiang, J. Electrochemical Soc., 143,1, 1-5, 1996



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‖ ($Li + H_2O + LiOH$)

Proyección de ventas de automóbiles eléctricos



Fuente: Roskill

CHAPTER 8

LITHIUM–AIR AND OTHER BATTERIES BEYOND LITHIUM-ION BATTERIES

K. M. Abraham

1 INTRODUCTION

The nonaqueous lithium–air battery, comprised of a lithium-metal anode and an oxygen cathode, is the highest-energy-density battery that can be developed into a practical system. It promises to overcome the energy density limitations of lithium-ion batteries, which have played an unequaled part in the modern electronic technology revolution. Lithium-ion batteries are indispensable in our everyday life as power sources for wireless telephones, laptop and tablet computers, music players, digital cameras, and many other consumer devices. The discovery of high-energy-density (energy stored per unit mass and volume) battery chemical couples based on Li intercalating negative and positive electrodes together with chemically and electrochemically compatible nonaqueous electrolytes, and engineering of the resulting Li-ion

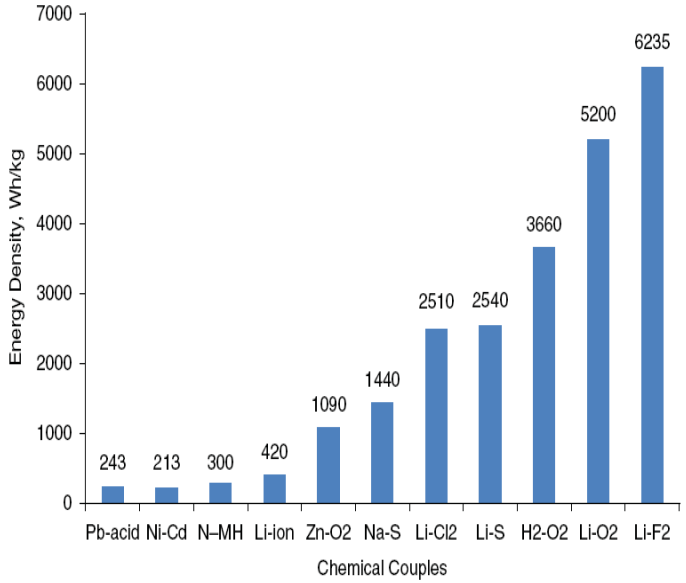


TABLE 1 Theoretical Voltages and Specific Energies of Metal–Air Batteries

Metal–air battery	Calculated OCV (V)	Theoretical specific energy (Wh/kg)	
		Including oxygen	Excluding oxygen
$Li–O_2$	2.91	5,200	11,140
$Na–O_2$	1.94	1,677	2,260
$Ca–O_2$	3.12	2,990	4,180
$Mg–O_2$	2.93	2,789	6,462
$Zn–O_2$	1.65	1,090	1,350

Lithium Batteries: Advanced Technologies and Applications, First Edition.
Edited by Bruno Scrosati, K. M. Abraham, Walter van Schalkwijk, and Jusef Hassoun.
 Published 2013 by John Wiley & Sons, Inc.

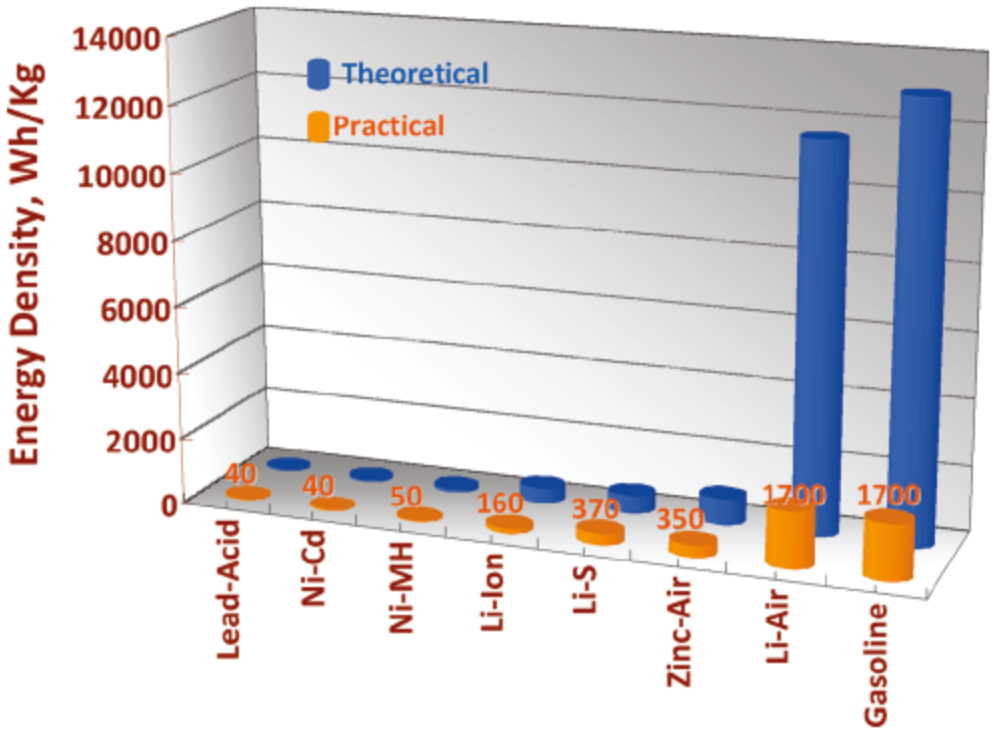


Figure 1. The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline. The theoretical density is based strictly on thermodynamics and is shown as the blue bars while the practical achievable density is indicated by the orange bars and numerical values. For Li—air, the practical value is just an estimate. For gasoline, the practical value includes the average tank-to-wheel efficiency of cars.

Representacion esquematica de celdas de:

ion-litio,

Li-O_2 no acuosa,

Li-O_2 acuosa,

Li-S

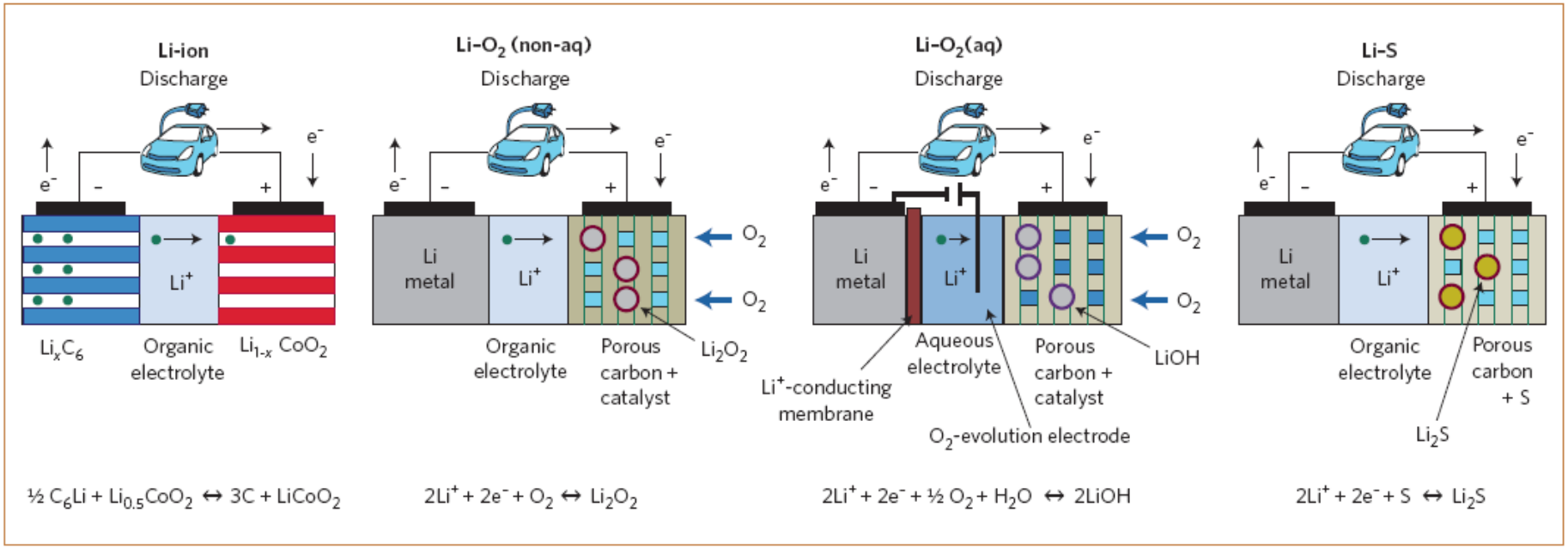
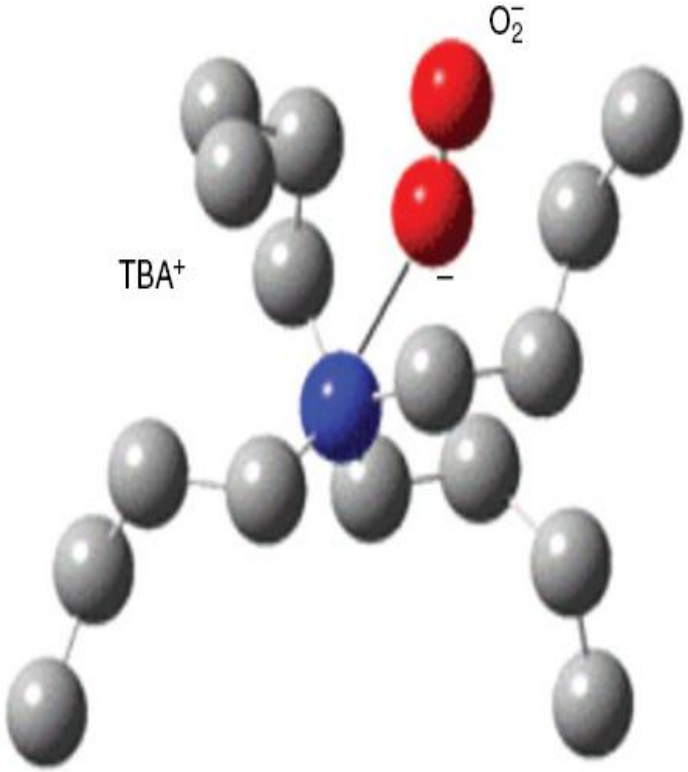
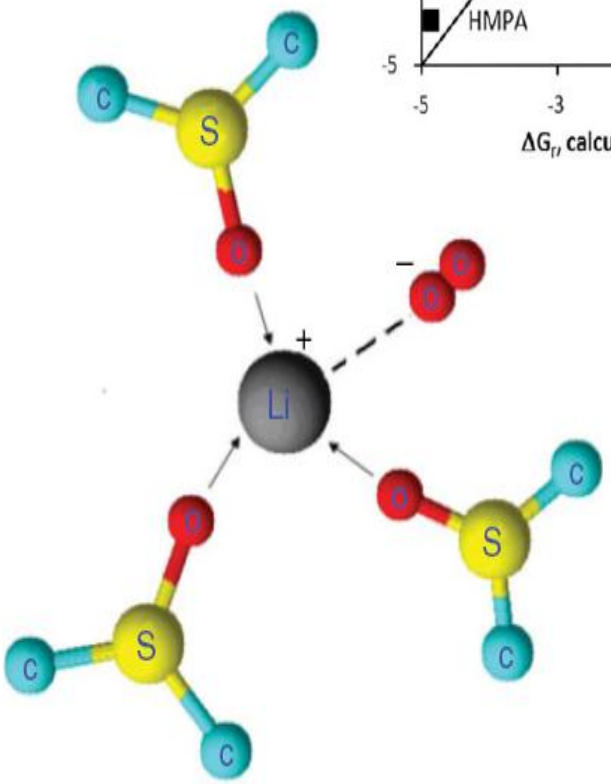
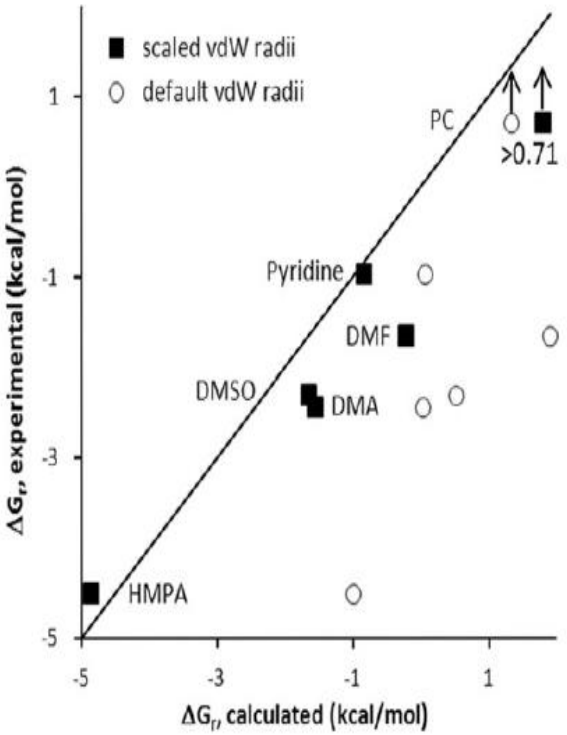


TABLE 2 Solvent Properties

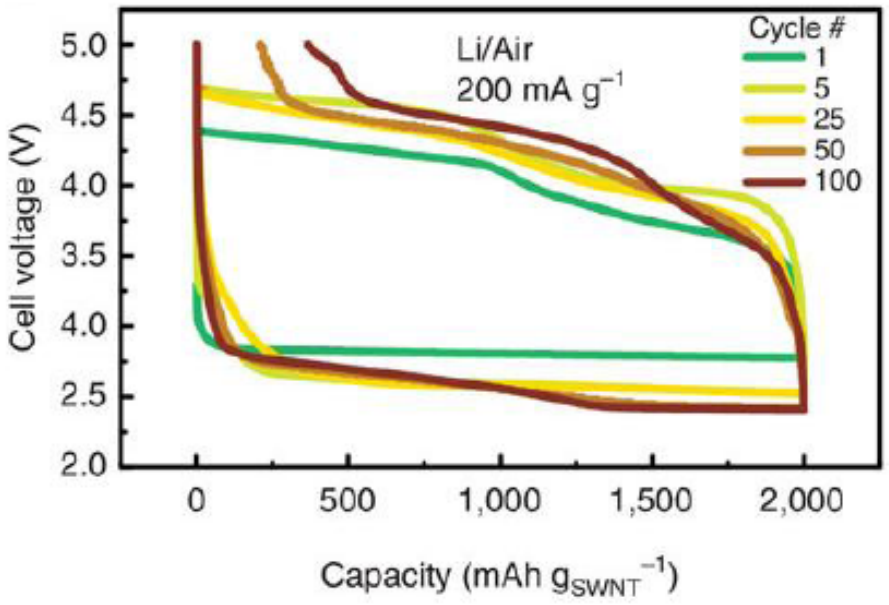
Solvent	ε 25°C	DN (kcal/mol)	Viscosity, η (cP)	Oxygen solubility (mM/cm^3)
Dimethyl sulfoxide	48.01	29.8	1.94	2.10
Acetonitrile	36.64	14.1	0.36	8.10
Tetraethylene glycol dimethyl ether	7.79	16.6	4.05	4.43
1,2-dimethoxyethane	7.20	20.0	0.46	9.57
Propylene carbonate	64.4	15.1	2.53	
Ethylene carbonate	89.6	16.4	1.85	1.55







High recharge overpotential and capacity fading upon cycling



Tao Zhang & Haoshen Zhou, *Nature Communications* 4, 1817, 2013

$$2\,Li + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2$$

Side reactions

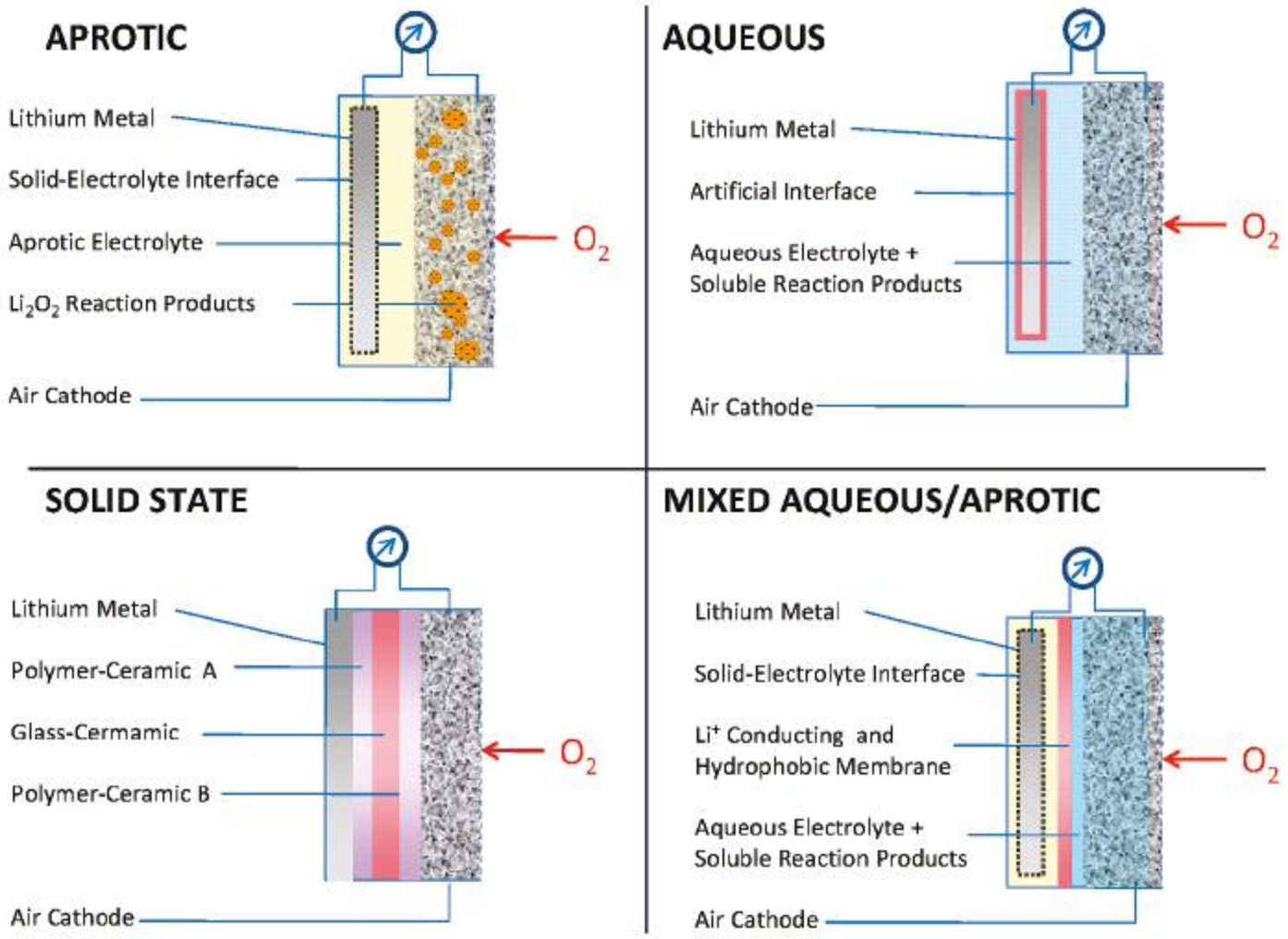
↓

Side products

↓

Loss of capacity

Distintas configuraciones de baterias de Li-aire



Ciclos de Carga-Descarga

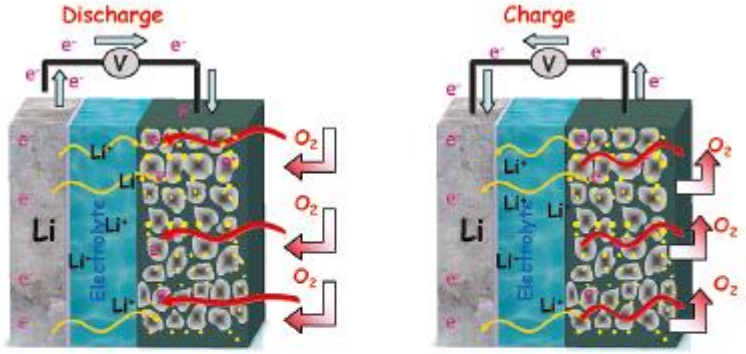
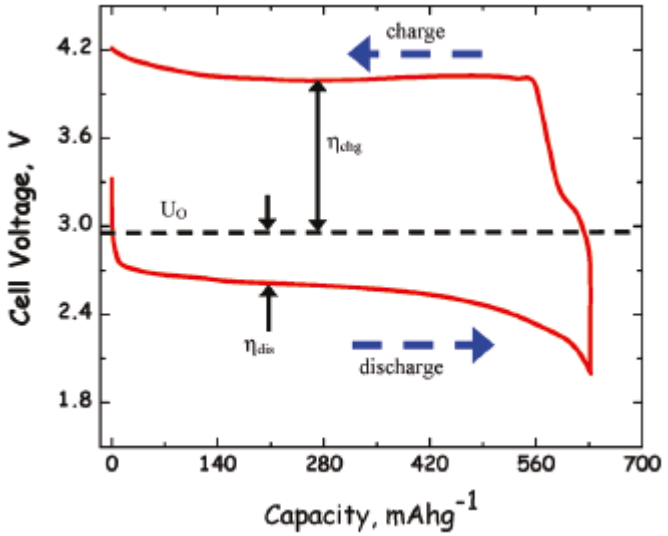
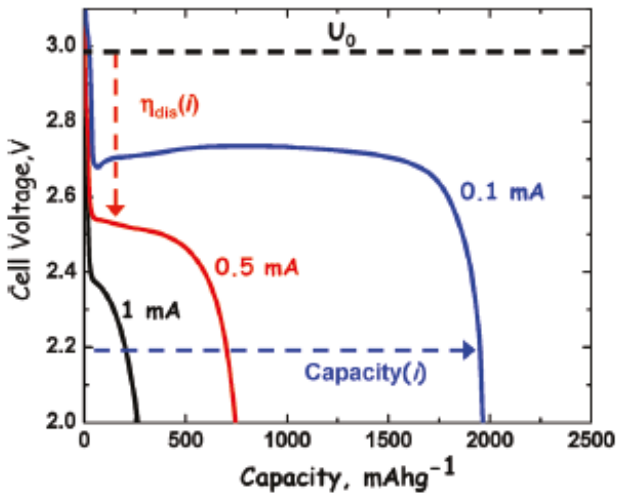


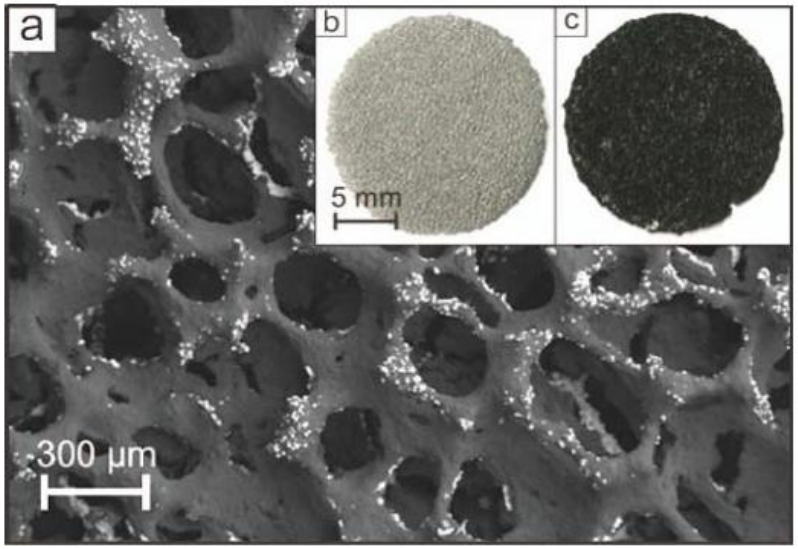
Figure 4. Schematic operation proposed for the rechargeable aprotic Li−air battery. During discharge, the spontaneous electrochemical reaction $2Li + O_2 \rightarrow Li_2O_2$ generates a voltage of 2.96 V at equilibrium (but practically somewhat less due to overpotentials). During charge, an applied voltage larger than 2.96 V (~4 V is required due to overpotentials) drives the reverse electrochemical reaction $Li_2O_2 \rightarrow 2Li + O_2$.

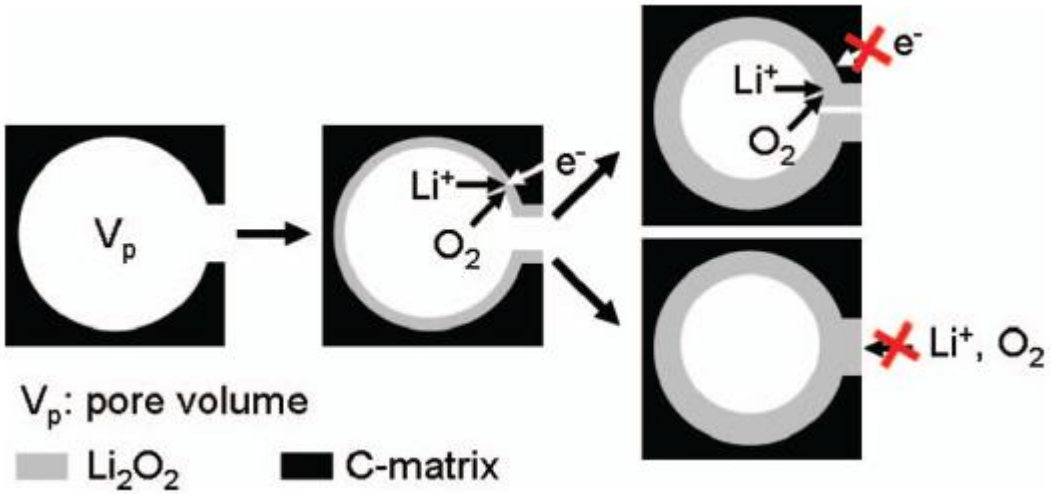
$$2(Li^+ + e^-) + O_2 \leftrightarrow Li_2O_2(solid)$$





ESTRUCTURA POROSA DEL CATODO DE CARBON





DESAFIOS TECNOLOGICOS

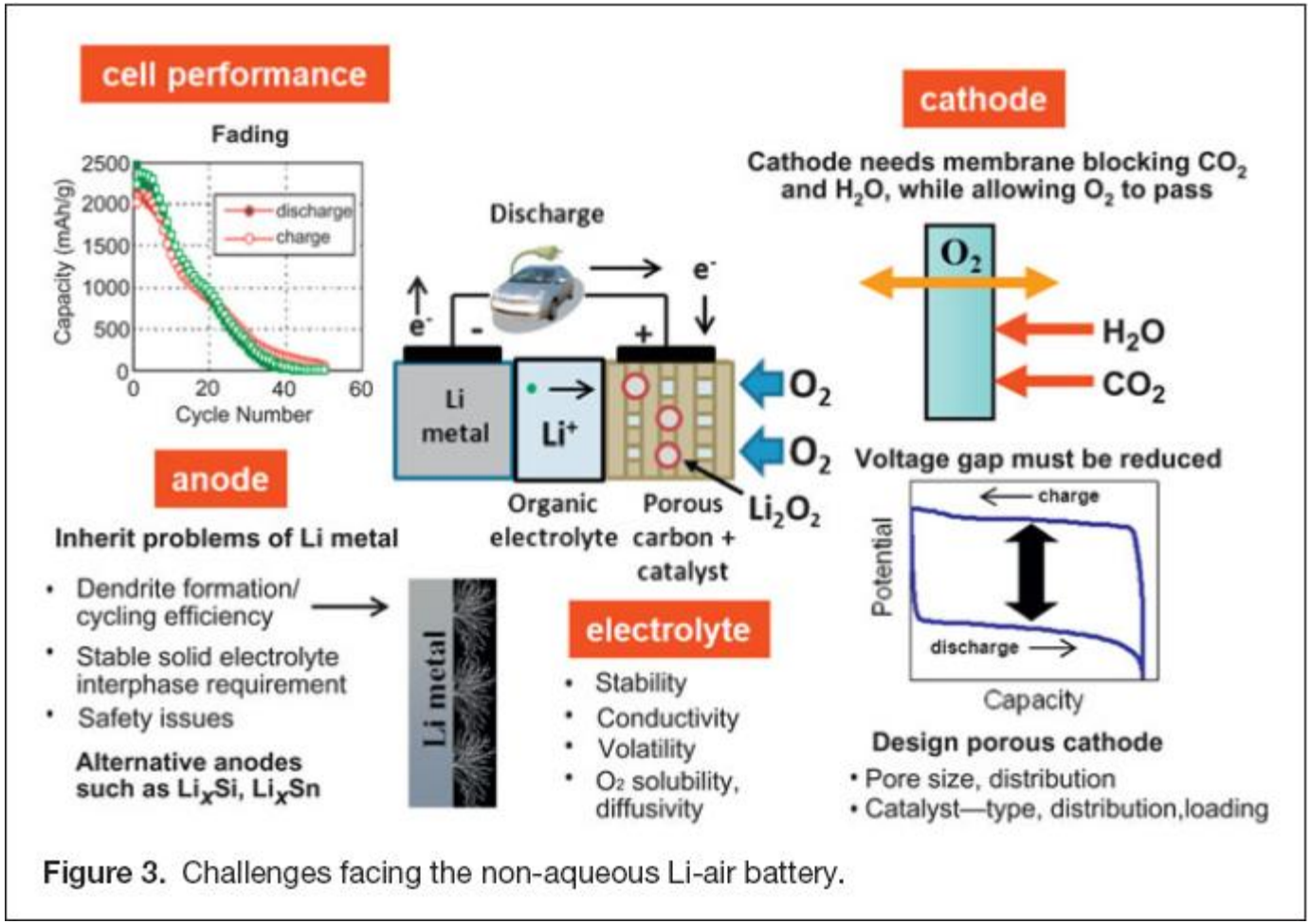


Figure 3. Challenges facing the non-aqueous Li-air battery.

Desafíos

- Baterías de Li-aire tienen mayor densidad gravimétrica de energía que $LiCoO_2$ (130 $mAh.g^{-1}$).
- Comprender las reacciones electroquímicas de carga-descarga.
- Desarrollar electrolitos resistentes a la oxidación en presencia de O_2 y Li_2O_2.
- Entender la naturaleza de electrocatálisis con la formación de productos insolubles (Li_2O_2).
- Desarrollar nuevas nanoestructuras de cátodos de aire para facilitar el transporte de O_2 y Li^+ .
- Mejorar las condiciones de ánodos de litio metálico para ciclos repetidos sin dendritas.
- Desarrollo de membranas permeables a O_2 del aire filtrando H_2O y CO_2

Lithium–Air Battery: Promise and Challenges

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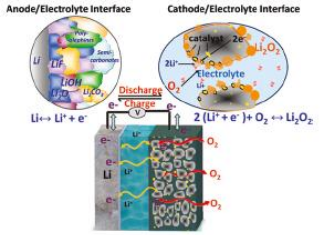

$$O_2 + e^- \rightarrow O_2^-$$

$$O_2^- + Li^+ \rightarrow LiO_2$$

$$2LiO_2 \rightarrow Li_2O_2 + O_2$$

Reducción electroquímica

$$LiO_2 + Li^+ + e^- \rightarrow Li_2O_2$$

$$Li_2O_2 + Li^+ + e^- \rightarrow 2Li_2O$$

Re oxidación del peróxido

$$Li_2O_2 \rightarrow 2Li^+ + 2e^- + O_2$$

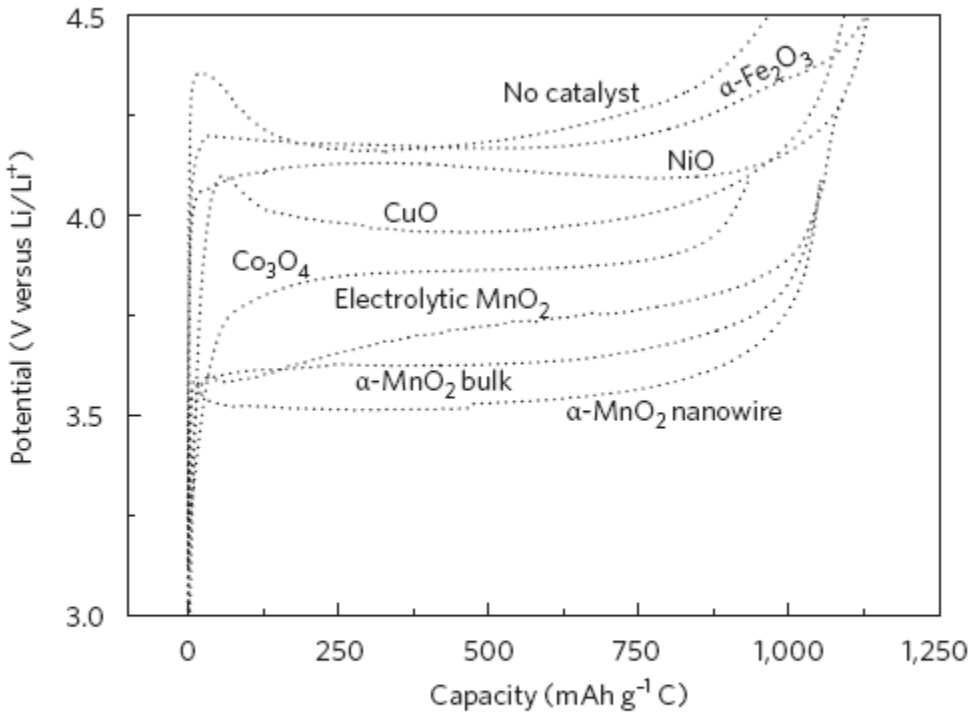

Figure 4 | First galvanostatic charge, $i = 70\,mA\,g^{-1}\,C$ (that is, Li_2O_2 oxidation) for various catalyst-containing Li–O_2 cells in this study[77].
Figure adapted with permission from ref. 77, © 2010 ECS.

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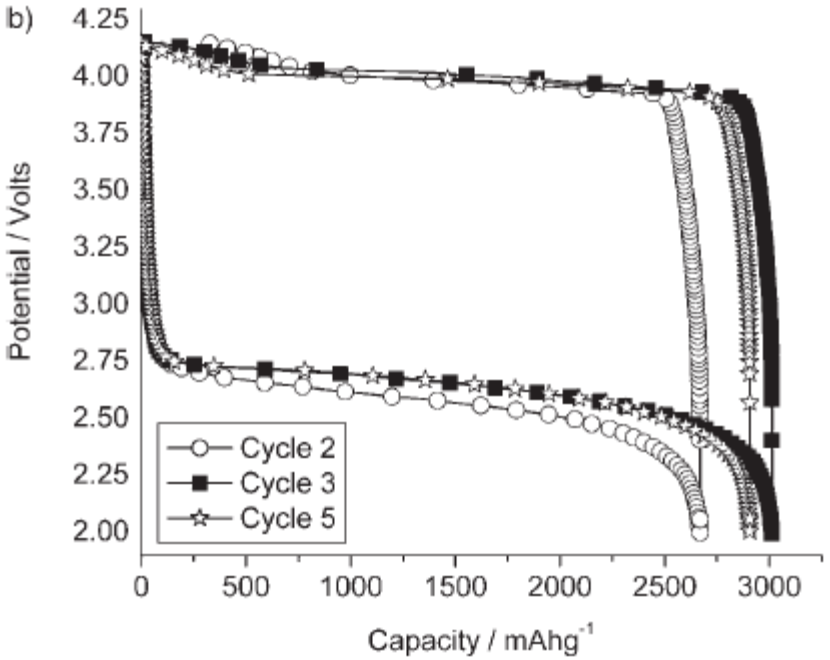
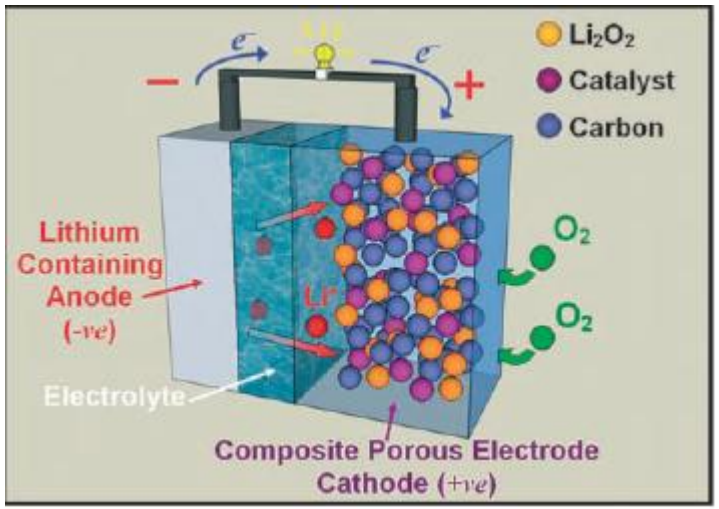
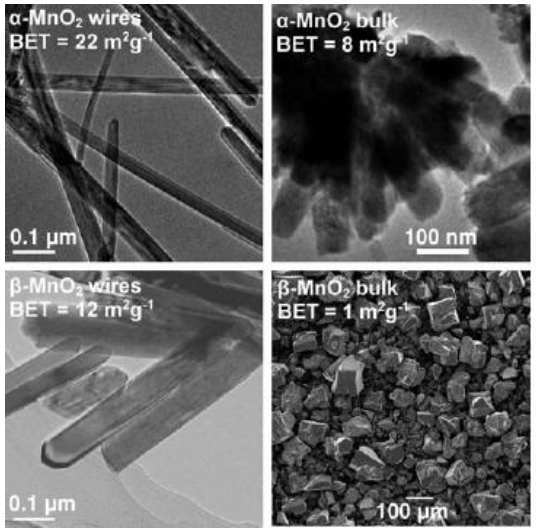
α-MnO_2 Nanowires: A Catalyst for the O_2 Electrode in Rechargeable Lithium Batteries**

*Aurélie Débart, Allan J. Paterson, Jianli Bao, and Peter G. Bruce**

Angew. Chem. Int. Ed. 2008, 47, 4521–4524







Platinum−Gold Nanoparticles: A Highly Active Bifunctional Electrocatalyst for Rechargeable Lithium−Air Batteries

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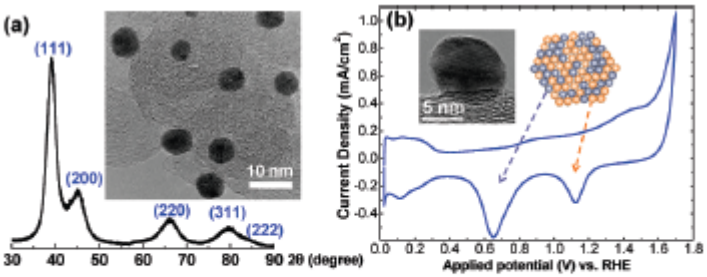

Figure 1. (a) Representative TEM image (top right) and XRD data of PtAu/C. (b) Cyclic voltammograms of PtAu/C collected in Ar-saturated 0.5 M H_2SO_4 between 0.05 and 1.7 V vs RHE (room temperature and 50 mV/s). Insets: (left) HRTEM image of PtAu/C and (right) schematic representation of PtAu, with arrows indicating the CV signatures for Pt (gray) and Au (yellow).