2021資源與環境學術研討會

日期：中華民國110年11月19日
時間：9:00~17:00
地點：大漢技術學院

主辦單位：大漢學校財團法人大漢技術學院
土木工程與環境資源管理系
協辦單位：國立成功大學奈米粉體科技研究中心
國立宜蘭大學環境工程學系
花蓮縣環境保護局
台泥企業集團
亞洲水泥股份有限公司花蓮製造廠
康廷工程顧問企業有限公司
日揚環境工程有限公司
亞太環境科技股份有限公司
祥威環境科技有限公司
新翊環境有限公司
春迪企業股份有限公司
承晏環境科技股份有限公司
長慧環境科技有限公司

目　　錄

2021 資源與環境學術研討會 程序表

110 年 11 月 19 日 (星期五)

時 間	議 程			引言人(主持人)
08：30 至 09：00	報到(土木館川堂)			
09：00 至 09：20	開 幕 貴賓致詞			王世忠 主任
09：20 至 10：20	專題演講 演講者：向性一 教授 演講題目：「廢棄鋰離子電池資源化技術」			胡紹華 教授
10：20 至 10：50	茶 敘(2F 走廊)			
10：50 至 12：00	Session I-1 (B215)	Session I-2 (B204)	Session I-3 (B219)	顏富士 向性一 陳智成
12：00 至 13：40	午 餐(B215、B204、B219)			
13：40 至 15：00	Session II-1 (B215)	Session II-2 (B204)	Session II-3 (B219)	余炳盛 蔡志達 何志軒
15：00 至 15：40	茶 敘(2F 走廊)			
15：40 至 17：00	Session III-1 (B215)	Session III-2 (B204)	Session III-3 (B219)	張章堂 林凱隆 謝哲隆
期待再重逢！				

2021 資源與環境學術研討會論文發表分組議程表

110 年 11 月 19 日 (星期五) 09:20～10:20

專題演講 B215

引言人：胡紹華 教授

演講者：向性一 教授（國立成功大學資源工程學系 系主任）

Session I-1 (10:50～12:00) B215

主持人：顏富士 教授（國立成功大學）

Session I-2 (10:50～12:00) B204

主持人：向性一 教授（國立成功大學）

Session III-2 (15:40～17:00) B204

主持人：林凱隆 教授 (國立宜蘭大學)

Session III-3 (15:40～17:00) B219

主持人：謝哲隆 教授 (國立宜蘭大學)

海報發表

專題演講

演講者：向性一 教授

演講題目:「廢棄鋰離子電池資源化技術」

廢棄鋰離子電池資源化技術

向性一
資源工程學系
國立成功大學

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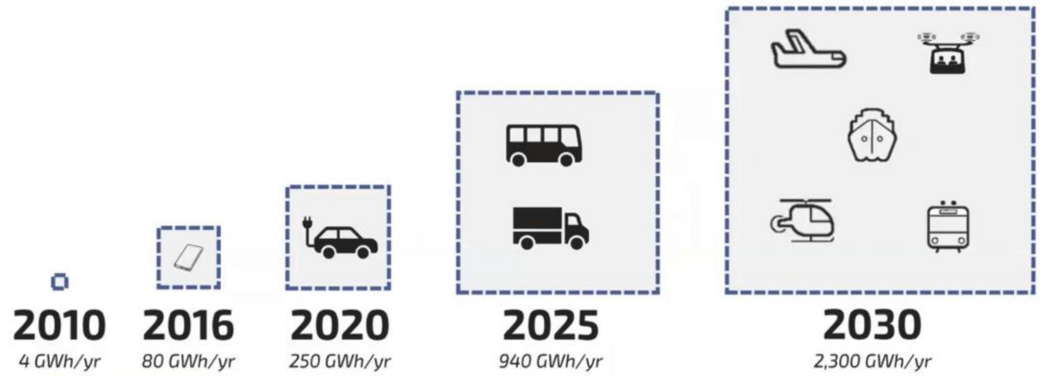
EXPONENTIAL LI-ION BATTERY DEMAND GROWTH

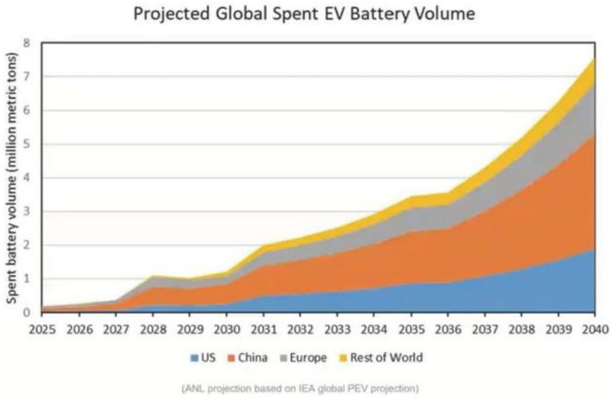
Lithium-ion battery demand globally has risen dramatically over the last 10 years, and is only beginning

Global demand depicted below with accurate relative scale



SETTING THE STAGE

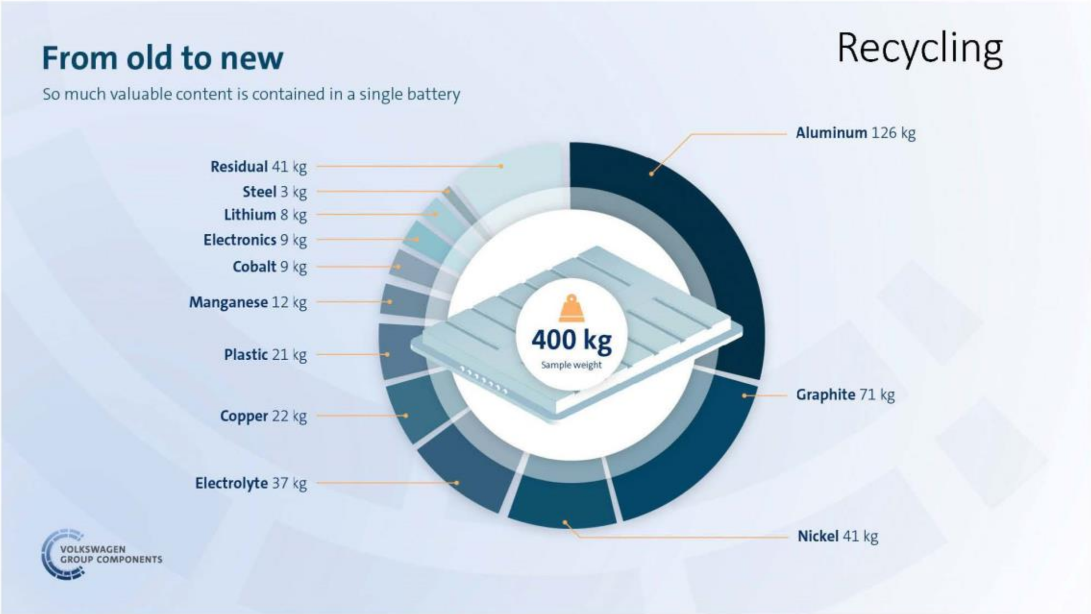
- An increase of lithium-ion batteries coming in electric vehicles (EV)
  - Consumer electronics collection is an issue
  - Stationary applications can be in remote locations
- Cannot meet EV material demand without recycling

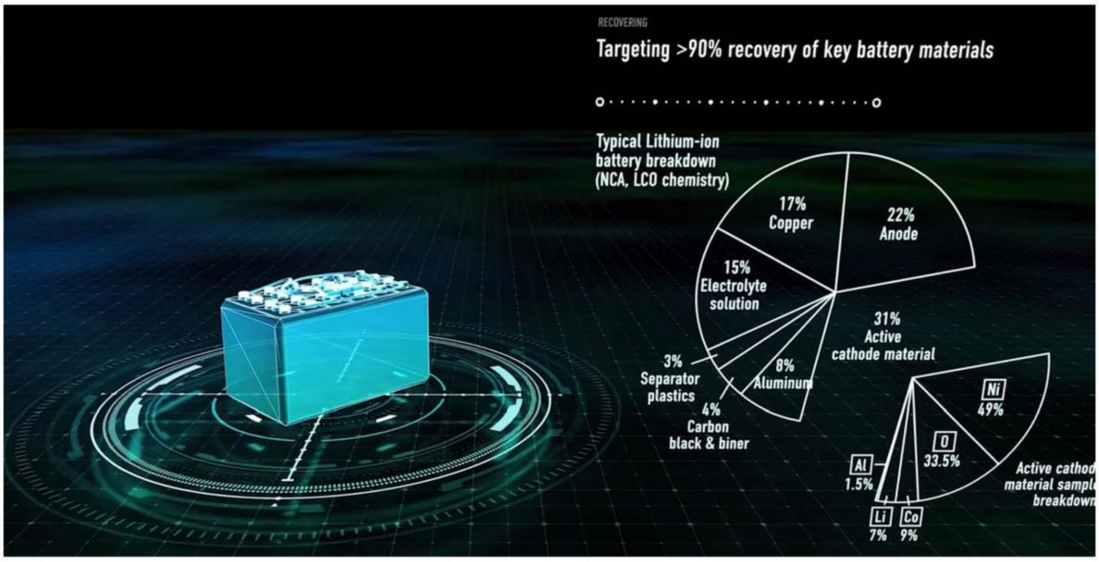


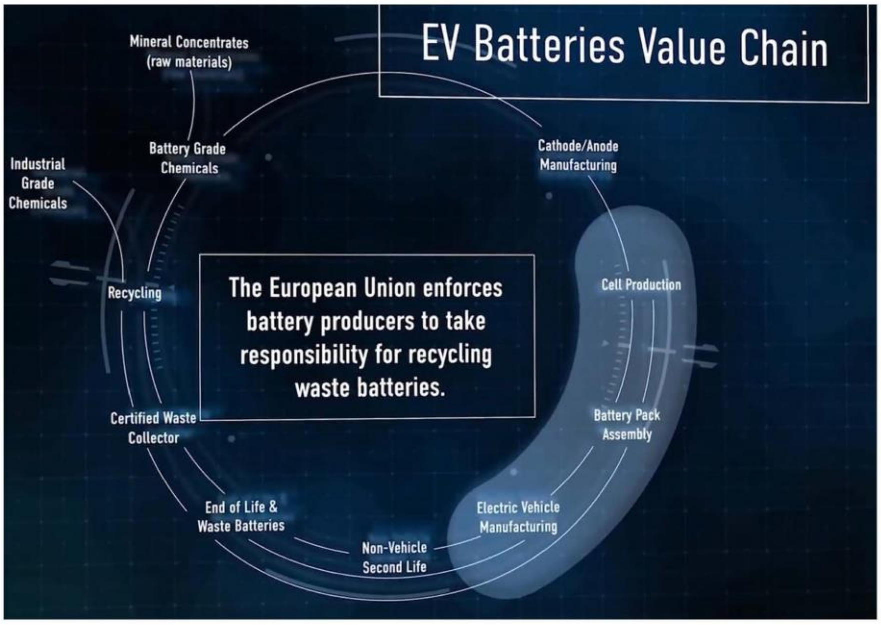
Types of LIBs in the market

	LCO - Lithium Cobalt Oxide	LFP - Lithium Iron Phosphate	LMO - Lithium Manganese Oxide	NCA - Lithium Nickel Cobalt Aluminium Oxide	NMC - Lithium Nickel Manganese Cobalt Oxide	LTO - Lithium Titanate
	$LiCoO_2$	$LiFePO_4$	$LiMn_2O_4$	$LiNiCoAlO_2$	$LiNiMnCoO_2$	Li_2TiO_3
Specific Energy, Wh/kg	150-200	90-120	100-150	200-260	150-220	50-80
Cycle Life	500-1,000	>2,000	300-700	500	1,000-2,000	3,000-7,000
Applications	Mobile phones, tablets, laptops, cameras	High load currents and endurance, E-buses, e.g. BYD	Power tools, medical devices, electric powertrains	Medical devices, industrial,electric powertrain, e.g. Tesla EV, Panasonic	E-bikes, medical devices, EV, e.g. Nissan LEAF, iMiEV, Volt	Uninterrupted power supply, electric powertrain

Source: Battery University


From old to new
So much valuable content is contained in a single battery
Recycling
Aluminum 126 kg
Residual 41 kg
Steel 3 kg
Lithium 8 kg
Electronics 9 kg
Cobalt 9 kg
Manganese 12 kg
Plastic 21 kg
Copper 22 kg
Electrolyte 37 kg
400 kg
Sample weight
Graphite 71 kg
Nickel 41 kg
VOLKSWAGEN
GROUP COMPONENTS


RECOVERING
Targeting >90% recovery of key battery materials
Typical Lithium-ion
battery breakdown
(NCA, LCO chemistry)
17%
Copper
22%
Anode
15%
Electrolyte
solution
31%
Active
cathode material
3%
Separator
plastics
8%
Aluminum
4%
Carbon
black & biner
Ni
49%
O
33.5%
Al
1.5%
Li
7%
Co
9%



Li-cycle

- https://youtu.be/-J8aMdxLZNI
- https://youtu.be/TeBf_ok5X_g

Closed Loop Resource Recovery

Industry-leading technology enabling a closed-loop economy.

Logistics Management

A reliable network of logistics partners to support customers in getting their batteries to our facilities.

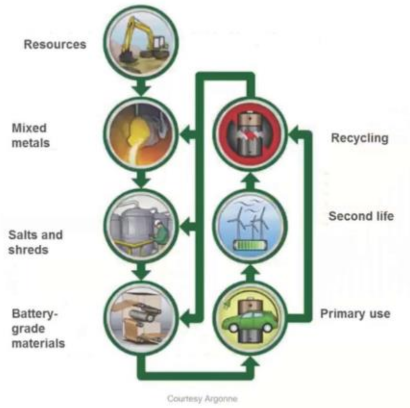
Secure Destruction

A home for the secure destruction of materials containing IP-sensitive design information.

Add-on Services

Additional services customized to meet our customers' needs

- Recycling lithium-ion batteries is possible today
- These processes are mature
- Produce lower value products and are not revenue positive without tipping fees for many chemistries



Current recycling process

Processing "black mass"

Comparison of main technologies

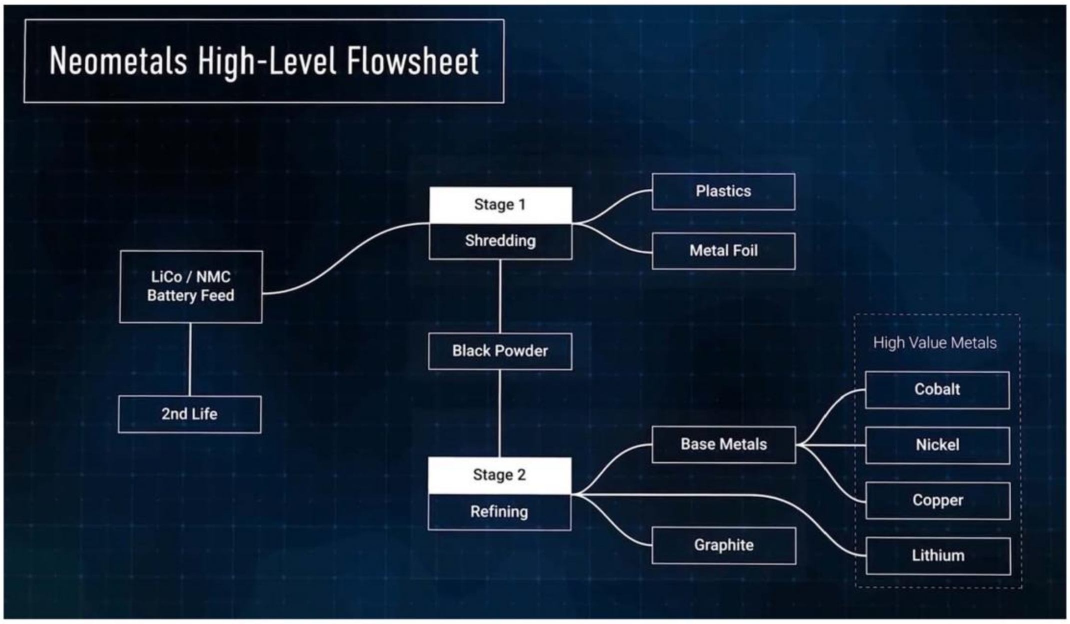
Pyrometallurgy

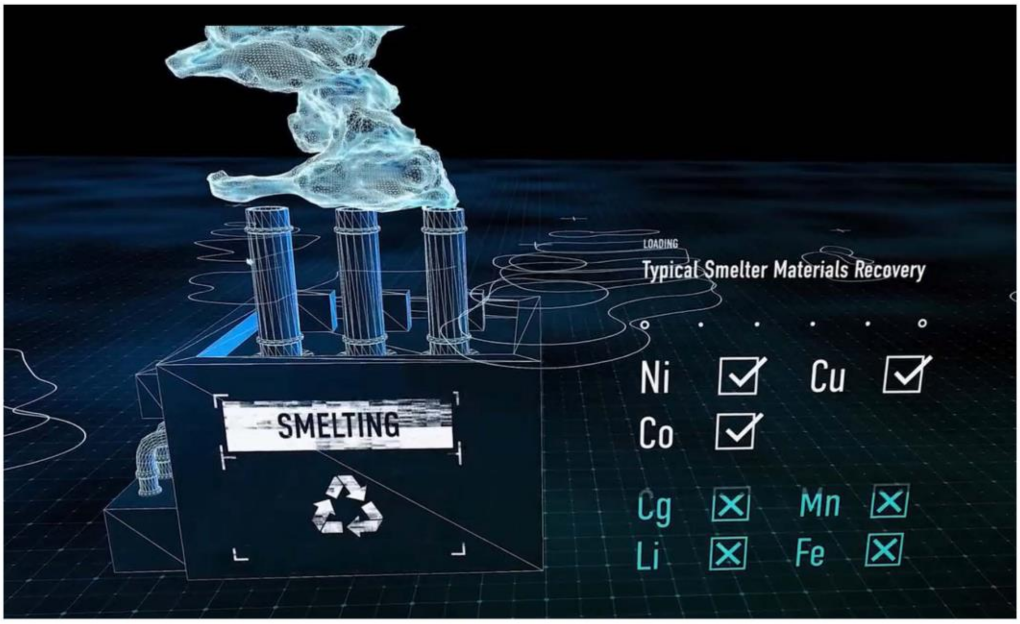
- ✓ High recovery rates for nickel, cobalt and copper
- ✓ Graphite and solvents burned, providing much of the process energy
- ✓ Mature technology
- ✕ High energy intensity (around 1,500°C) and CO_2 footprint
- ✕ Loss of lithium in slag – recovery from slag is expensive

Hydrometallurgy

- ✓ High recovery rates for cobalt, nickel and copper
- ✓ Lithium is recycled
- ✓ Option for manganese and graphite recycling
- ✓ Moderate temperature range
- ✕ High investment required
- ✕ Inflexible process
- ✕ High amounts of by-products, waste

Both technologies call for improvements towards lithium yield, by-products or investment cost.


Neometals High-Level Flowsheet
LiCo / NMC Battery Feed
2nd Life
Stage 1
Shredding
Plastics
Metal Foil
Black Powder
Stage 2
Refining
Base Metals
Graphite
High Value Metals
Cobalt
Nickel
Copper
Lithium


SMELTING
LOADING
Typical Smelter Materials Recovery
Ni
Cu
Co
Cg
Mn
Li
Fe

RECYCLING SUPPLY CHAIN: INCUMBENT PROCESS

Incumbent recycling chain/processes

Disaggregated, inefficient, low recoveries, waste-oriented

≤50% recovery rate

Batteries received, discharged, dismantled heavily, potentially shredded

High temperature processing, calcining / roasted, burning off electrolyte, plastics, and other volatile components

Smelter – electric furnace process, processes black mass from the preceding step

Traditional hydromet refinery; processes the matte containing Ni, Co, Cu from the electric furnace; produces Ni, Co, Cu metal

Re-dissolve metals to produce Co & Ni chemicals (sulphates) that can be utilized by typical cathode precursor manufacturers

What's being lost:

Possibly the electrolyte; partially the plastics	*Electrolyte lost; fluorine emitted; potentially plastics; potentially graphite*	*Lithium goes into slag (uneconomic to recover thereafter); graphite, aluminum, and other light components – all directed to the slag and off-gas*	*Losing any residual manganese and other minor components in the matte from the smelter*	*N/A*

Spoke & Hub Technologies

A combination of mechanical safe size reduction and hydrometallurgical resource recovery specifically designed for lithium-ion battery recycling.

95% recovery

MECHANICAL SAFE SIZE REDUCTION

Spoke

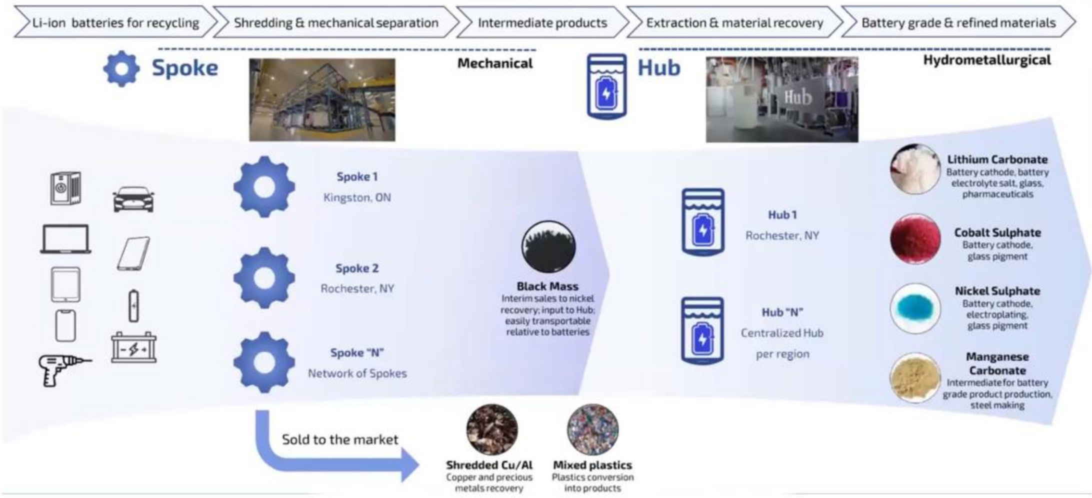
All types of lithium-ion batteries are transformed from a charged state to an inert product in a safe and efficient manner.

HYDROMETALLURGICAL PROCESSING

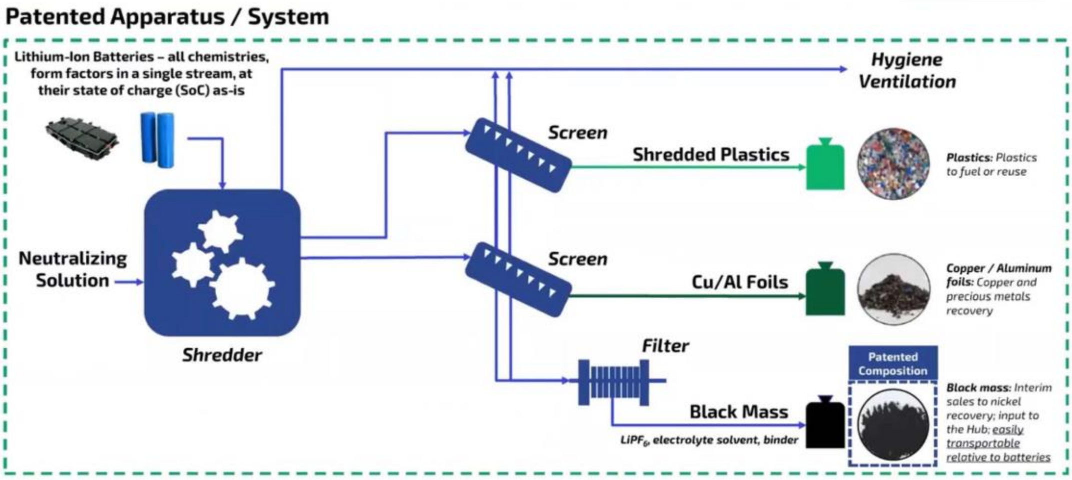
Hub

Cathode and anode materials are processed into battery grade end-products for reuse in lithium-ion battery production or other applications in the broader economy.

Spoke and Hub Technology of Li-Cycle

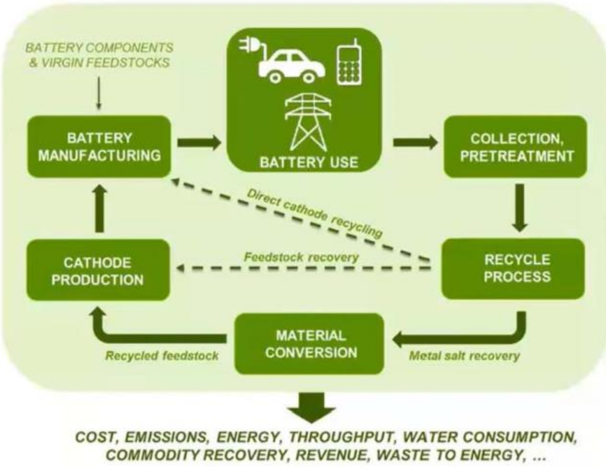


Spoke Technology



Shredding-drying-sieving-magnetic separating-electric separating 分選為塑料、鋁銅、電極粉末

Closed loop of Lithium battery

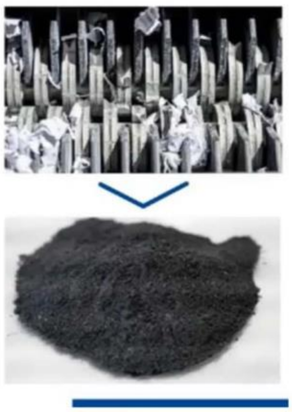


“Black mass*” – a new resource

- Recycling of lithium-ion batteries (LIB) starts with mechanical operations (e.g., dismantling, shredding, sorting).
- This yields “black mass”.
- It mainly consists of the electrode active material.
- Black mass contains valuable Co, Ni, Mn, Li, but also carbon and many contaminants.

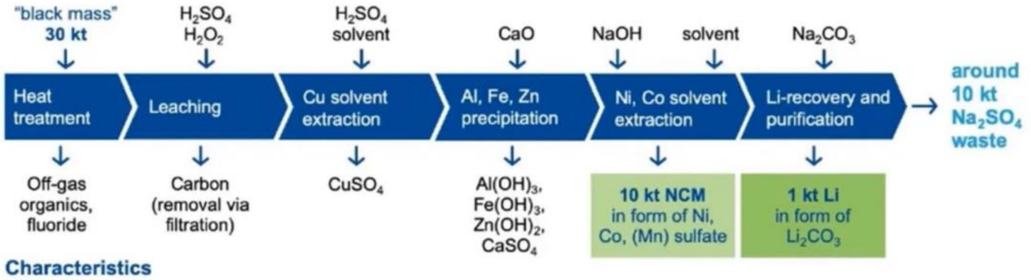
Chemical treatments are needed to extract the valuable metals from “black mass”.

	Element	Content
		weight %**
valuable metals	Ni	20
valuable metals	Co	6
valuable metals	Mn	6
valuable metals	Li	3.5
	C	40
	F	3
	P	0.5
	Cu	2
	Al	2
	Fe	1
	Zn	0.1
	Ca	0.1



Deep dive hydrometallurgy

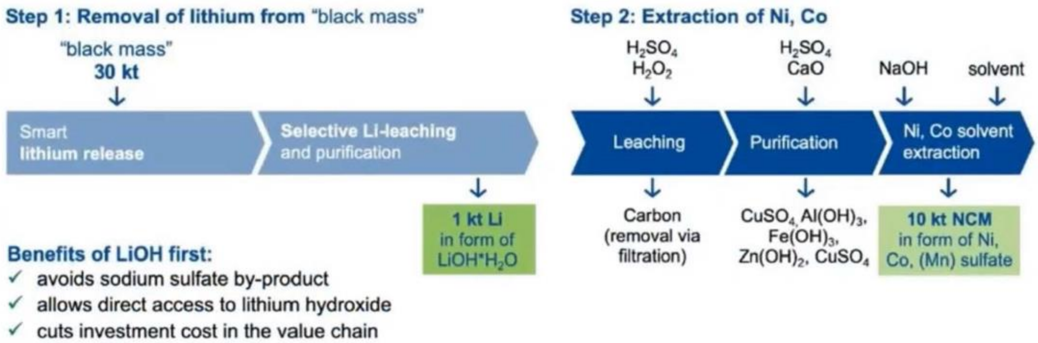
Illustrative process

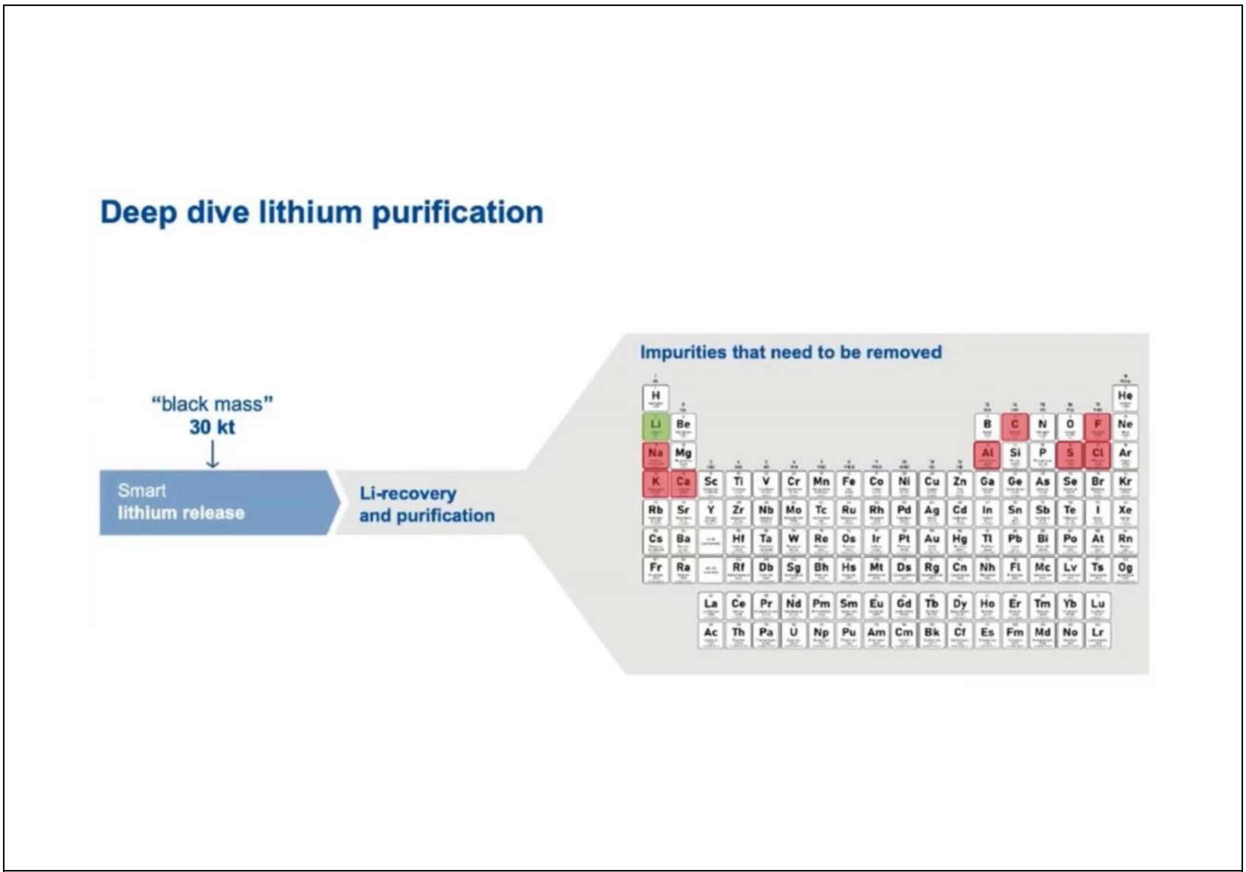


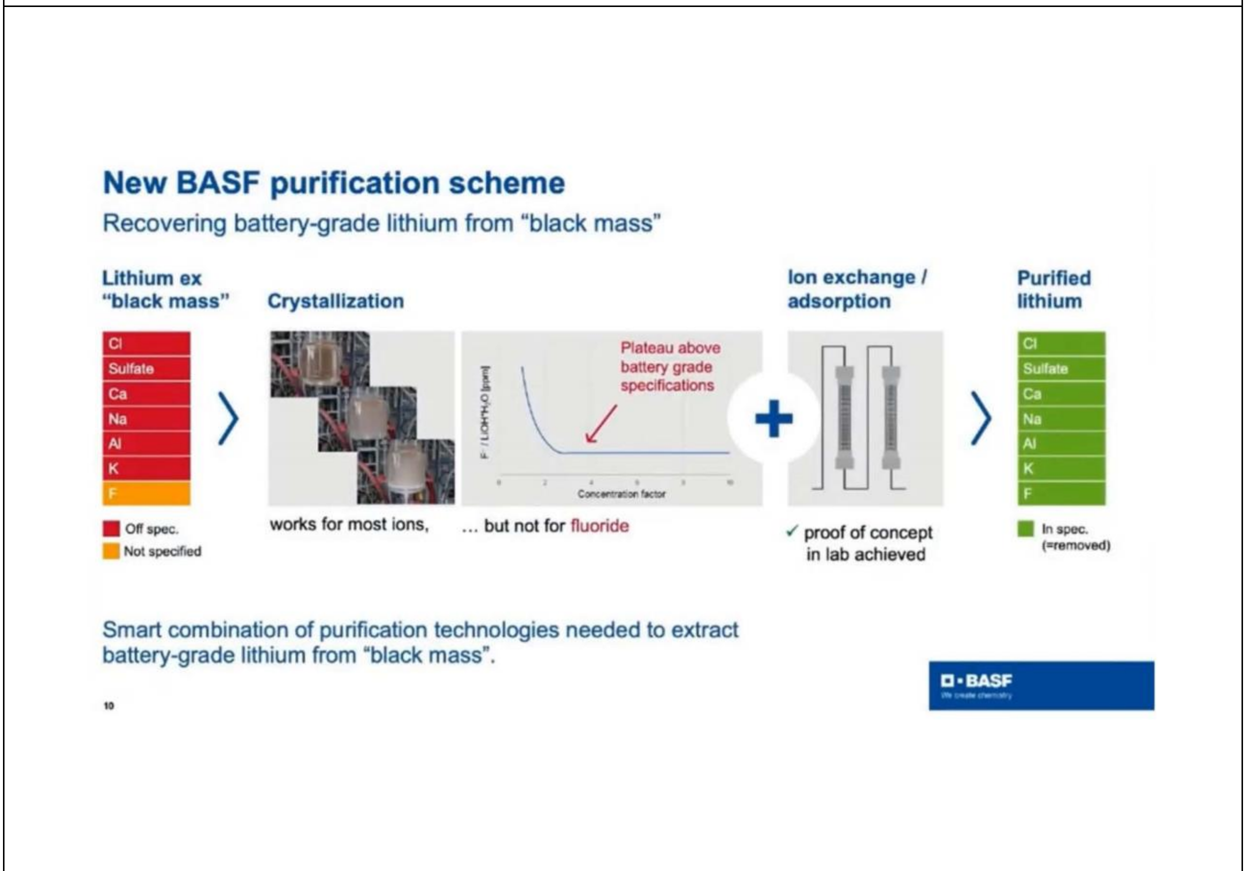
Characteristics

- ✓ Well established processes in mining industry up to nickel and cobalt recovery to build on
- × Inflexible process – lithium is always recycled at the end and comes as lithium carbonate only
- × Significant amounts of sodium sulfate waste by-product

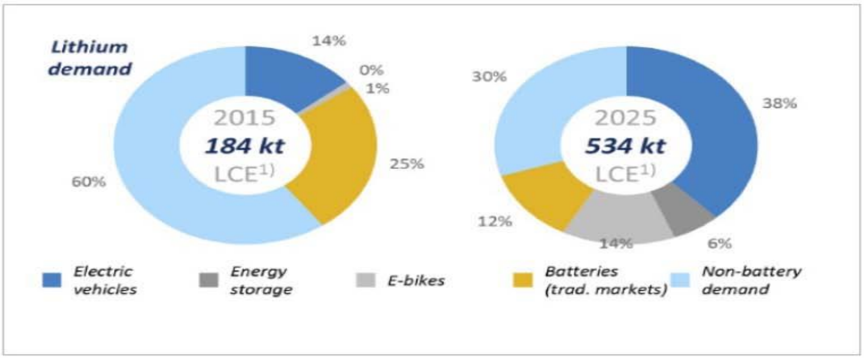
The process cuts CO_2 emissions by -25% vs. CAM* materials based on mining.




Deep dive lithium purification
"black mass"
30 kt
Smart
lithium release
Li-recovery
and purification
Impurities that need to be removed


New BASF purification scheme
Recovering battery-grade lithium from "black mass"
Lithium ex
"black mass"
Cl
Sulfate
Ca
Na
Al
K
F
Off spec.
Not specified
Crystallization
Plateau above
battery grade
specifications
Concentration factor
works for most ions,
... but not for fluoride
Ion exchange /
adsorption
✓ proof of concept
in lab achieved
Purified
lithium
Cl
Sulfate
Ca
Na
Al
K
F
In spec.
(=removed)
Smart combination of purification technologies needed to extract
battery-grade lithium from "black mass".
10
BASF

Lithium demand



It suggest that the lithium demand strongly depends on the automotive electrification.

(Source: McKinsey, Bloomberg New Energy Finance, Deutsche Bank, Wealth Minerals)

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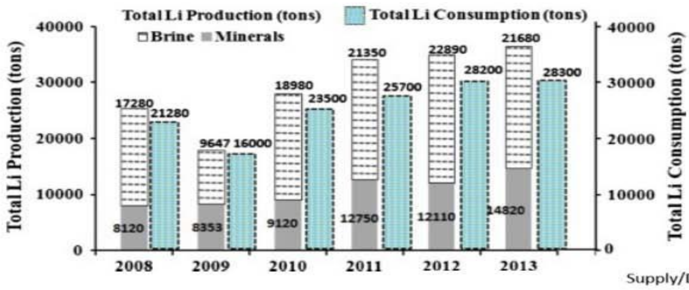
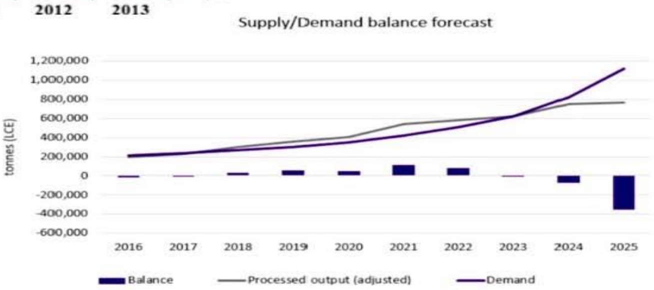
Demand and supply of lithium



Lithium dissolved in brines accounts for more than 66 % of global lithium reserves.

Today, most of the lithium is produced (about 83 %) from brines.



The deficiency of lithium carbonate will reach about 350 k tons.

1

Two main recovery resources of lithium

- Brine water
- Spent lithium battery

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Sustainability: the choice

To produce
1 Ton of Lithium
We need

250 T of ore
(spodumène)

Or
750 T of brines

28 T of Li ion batteries
from mobiles/laptops

Or 256 batteries
for EV

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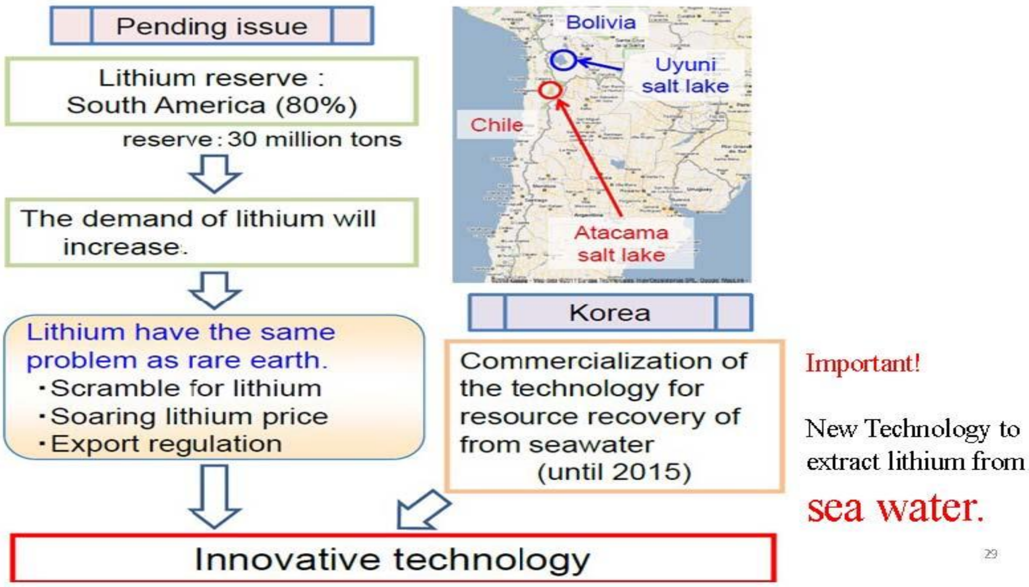
Pending issue
Lithium reserve :
South America (80%)
reserve : 30 million tons
The demand of lithium will increase.
Lithium have the same problem as rare earth.
・Scramble for lithium
・Soaring lithium price
・Export regulation
Bolivia
Uyuni salt lake
Chile
Atacama salt lake
Korea
Commercialization of the technology for resource recovery of from seawater
(until 2015)
Innovative technology
Important!
New Technology to extract lithium from
sea water.
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- Seawater Lithium Recovery Project
Illustrations of Lithium Recovery Plant
국토해양부
KIGAM 한국지질자원연구원
LITHIUM RECOVERY PLANT
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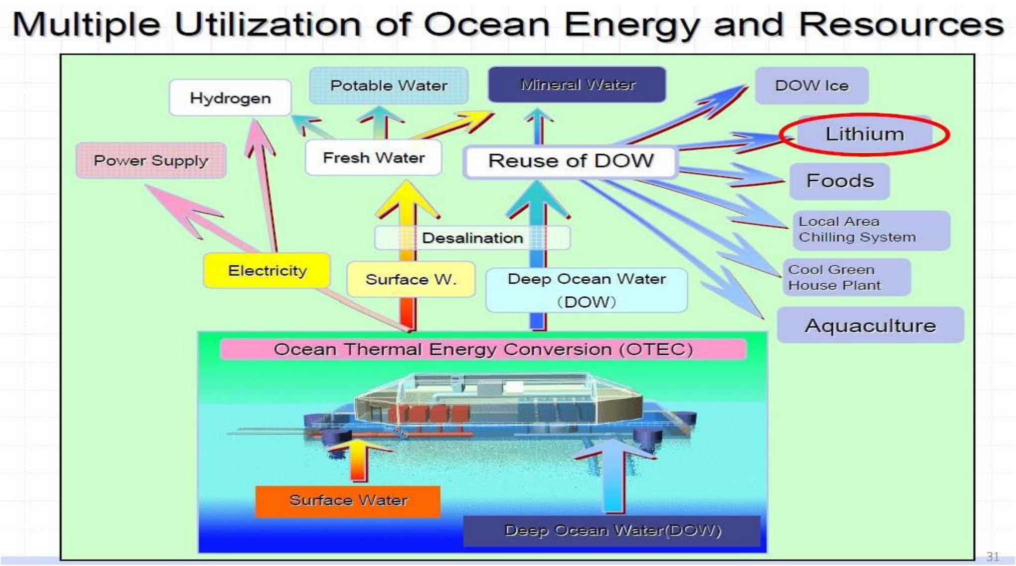
Multiple Utilization of Ocean Energy and Resources
Hydrogen
Potable Water
Mineral Water
DOW Ice
Lithium
Power Supply
Fresh Water
Reuse of DOW
Foods
Desalination
Local Area
Chilling System
Electricity
Surface W.
Deep Ocean Water
(DOW)
Cool Green
House Plant
Aquaculture
Ocean Thermal Energy Conversion (OTEC)
Surface Water
Deep Ocean Water(DOW)
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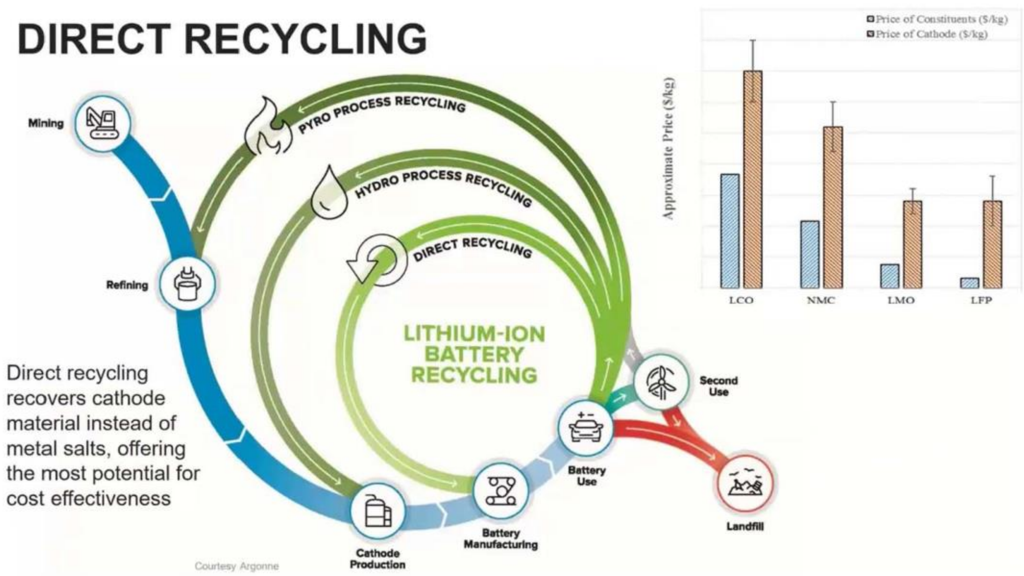
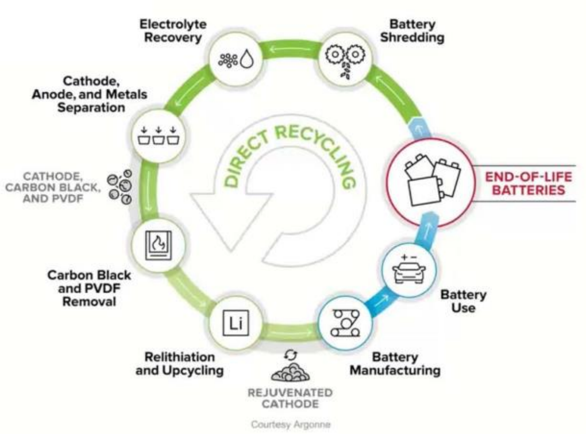

DIRECT RECYCLING
Mining
Refining
PYRO PROCESS RECYCLING
HYDRO PROCESS RECYCLING
DIRECT RECYCLING
LITHIUM-ION
BATTERY
RECYCLING
Second
Use
Battery
Use
Landfill
Battery
Manufacturing
Cathode
Production
Direct recycling
recovers cathode
material instead of
metal salts, offering
the most potential for
cost effectiveness
Courtesy Argonne
Price of Constituents ($/kg)
Price of Cathode ($/kg)
Approximate Price ($/kg)
LCO
NMC
LMO
LFP

DIRECT RECYCLING

- Multiple processes investigated to mitigate risk
- Continual review of new project ideas
- End projects that are not showing promise in cost and performance
- These unit operations can benefit other recycling processes

Typical Direct Recycling Process Flow



Cathode recovery could enable economical recycling

- Value of constituents for $LiFePO_4$ is low comparing with $LiCoO_2$ or $Li(Co,Ni,Mn)O_2$, but cathode itself has high value.

Cathode	Price of Constituents ($/lb)	Price of Cathode ($/lb)
$LiCoO_2$	$9.90	12.00[3,4]
$LiNi_{.3}Co_{.3}Mn_{.3}O_2$	$6.10	$8.80[4]
$LiMnO_2$	$1.35	$4.50[2]
$LiFePO_4$	$0.75[1]	$9.10[2]

Spent $LiFePO_4$ battery will not be recycled to the constituents by using chemical or high temperature smelting processes due to the lack of economic benefits.

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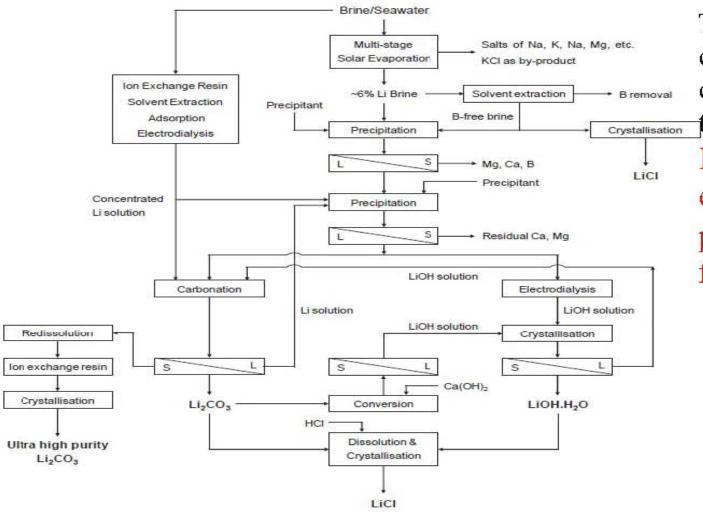
General flow sheet for production of lithium compounds from brines and seawater.



The traditional process is complex and needs many chemicals, which is detrimental to the environment.

Is there other simple and environmental friendly process to extract lithium from sea water?

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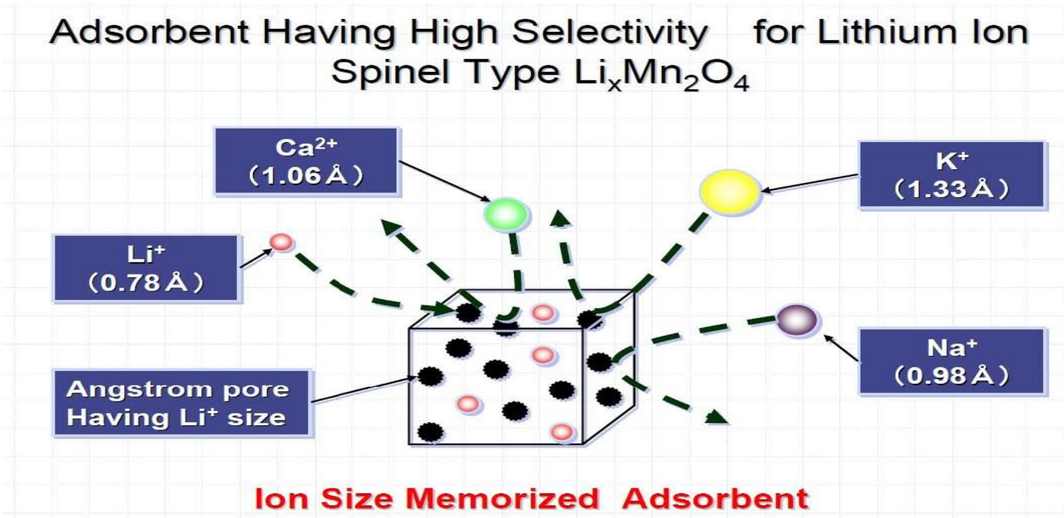

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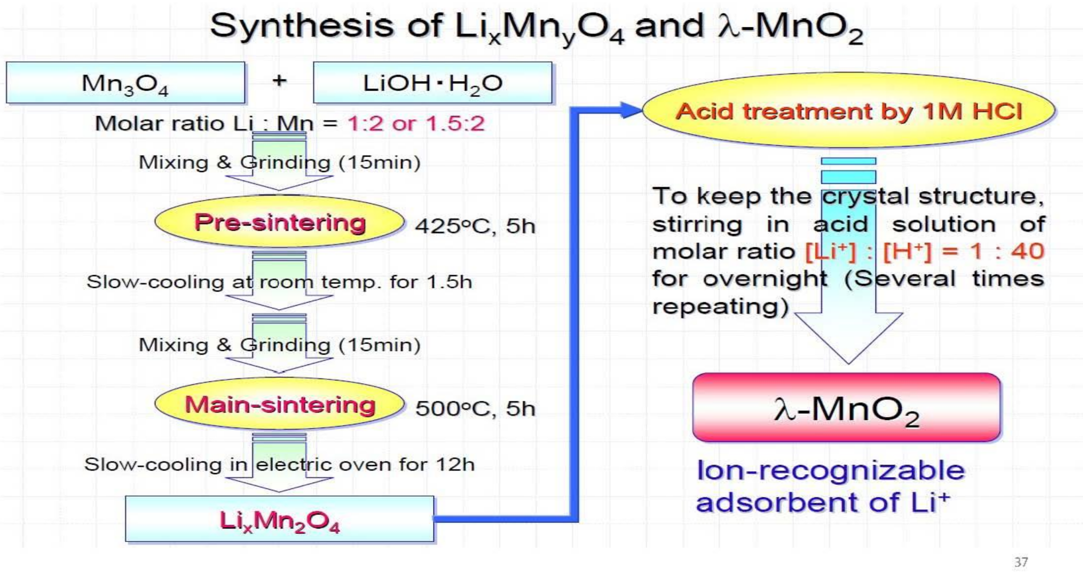
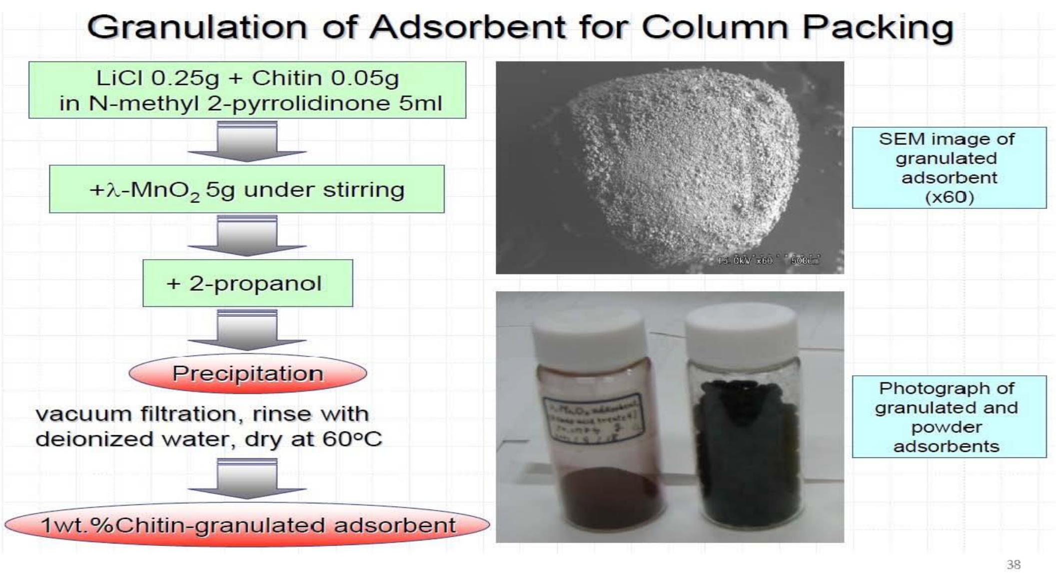
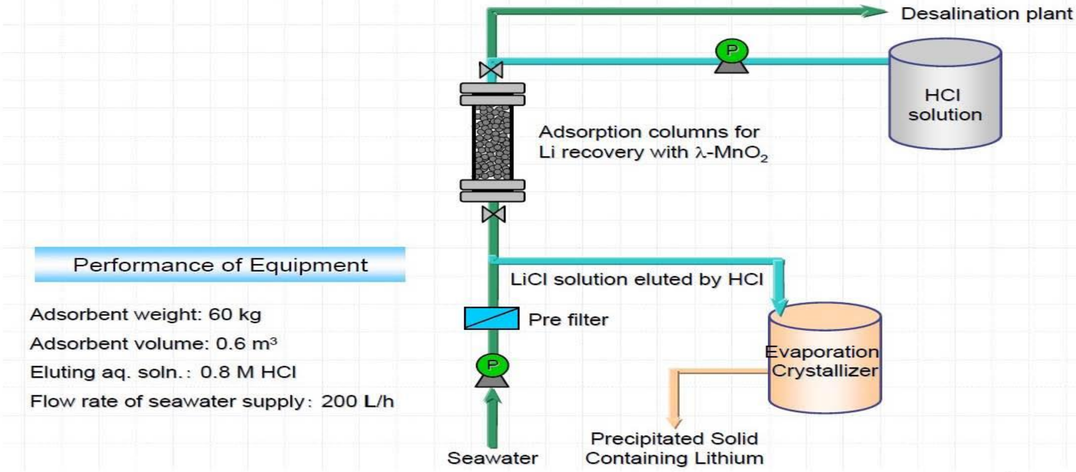

Synthesis of $Li_xMn_yO_4$ and λ-MnO_2
Mn_3O_4
+
$LiOH \cdot H_2O$
Molar ratio Li : Mn = 1:2 or 1.5:2
Mixing & Grinding (15min)
Pre-sintering
425°C, 5h
Slow-cooling at room temp. for 1.5h
Mixing & Grinding (15min)
Main-sintering
500°C, 5h
Slow-cooling in electric oven for 12h
$Li_xMn_2O_4$
Acid treatment by 1M HCl
To keep the crystal structure, stirring in acid solution of molar ratio $[Li^+] : [H^+] = 1 : 40$ for overnight (Several times repeating)
λ-MnO_2
Ion-recognizable adsorbent of Li^+
37


Granulation of Adsorbent for Column Packing
LiCl 0.25g + Chitin 0.05g
in N-methyl 2-pyrrolidinone 5ml
+λ-MnO_2 5g under stirring
+ 2-propanol
Precipitation
vacuum filtration, rinse with
deionized water, dry at 60°C
1wt.%Chitin-granulated adsorbent
SEM image of
granulated
adsorbent
(x60)
Photograph of
granulated and
powder
adsorbents
38

Benchmark Plant of Lithium Recovery from Seawater in IOES



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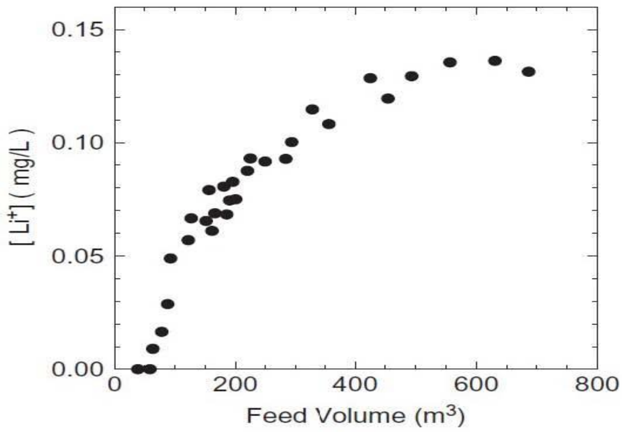

Lithium concentration profile after passing adsorption column.

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Ionic adsorption selectivity of MnO_2

Table 1. Metal composition of the eluted solution and the dried precipitate salt

Element	Eluted solution (mg/L)	Precipitated salt* (wt%)	Concentration efficiency from seawater
Li^+	160	33.3	11000
Na^+	236	20.4	0.26
K^+	92	3.3	0.94
Mg^{2+}	17	8.2	0.57
Ca^{2+}	176	13.4	4.11
Sr^{2+}	35	2.0	50
Mn^{2+}	234	19.4	–

*calculated as metal chlorides existing in the precipitates

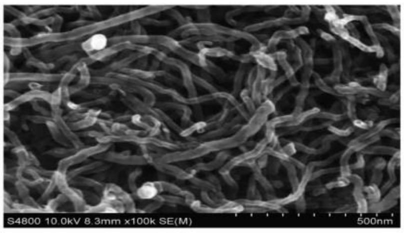
41

Problem of the ion sieve adsorption technology

- The main problem of the ion sieve adsorption technology: The adsorption capacity and rate became smaller and slower after granulation and adsorbent loss increased due to the degradation of the binder.

42

Electrosorption of LiCl in different solvents by carbon nanotube film electrodes



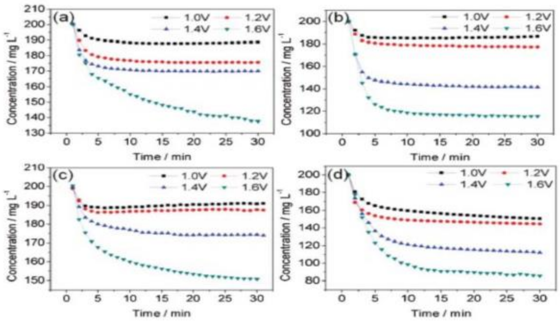


Fig. 2 Time-dependant LiCl concentration variation in (a) water, (b) methanol, (c) ethanol and (d) DMF during the electrosorption at different voltages.

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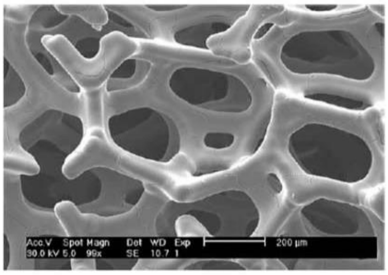
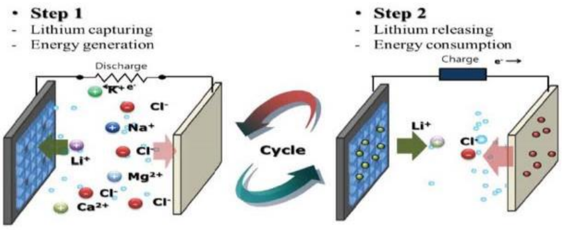
Purpose of research

Lithium ion sieve



\+

Electro-adsorption



Methodolgy: The spent $LiFePO_4$ powder was coated onto the surface of titanium mesh by using electrophoresis to form a 3D nano-structured electrode, which can extract lithium from brine water via electro-adsorption process.

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Benefits of the combination of 3-D nanostructured lithium ion sieve and electrosorption

- Fast adsorption/desorption rate due to the combination of the 3D nanostructure, lithium ion sieve and electric field.
- No need of granulation.
- No need of membrane which is expensive, easily leads to biofouling and is easily permanently destroyed by certain solvents and colloidal solids.
- No need of washing acid, which is more environmentally friendly.

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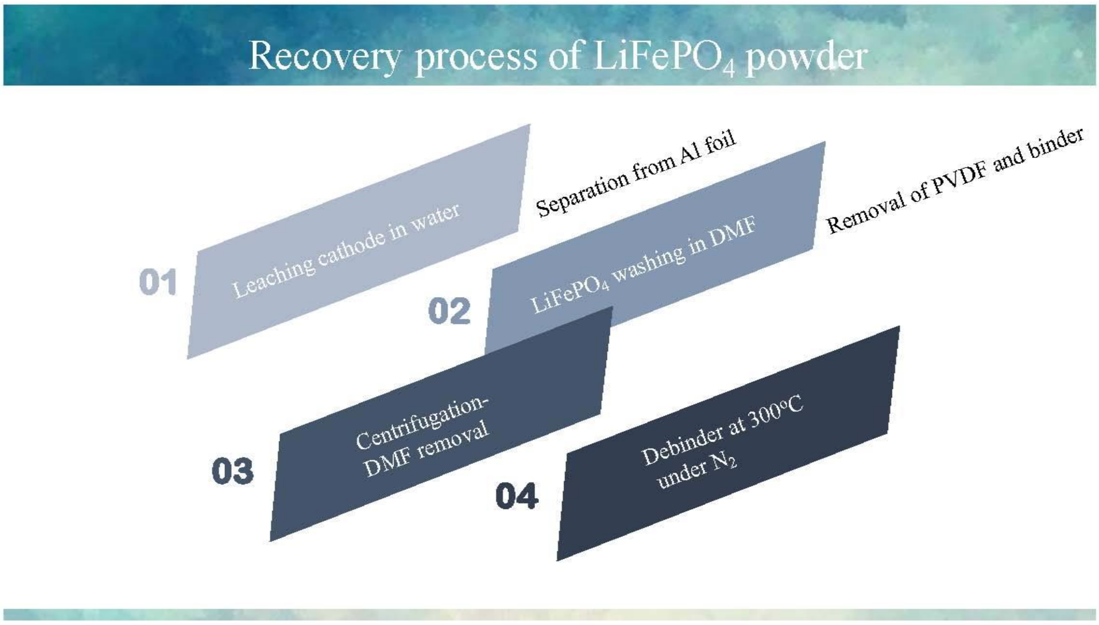
Disassembly of spent $LiFePO_4$ battery

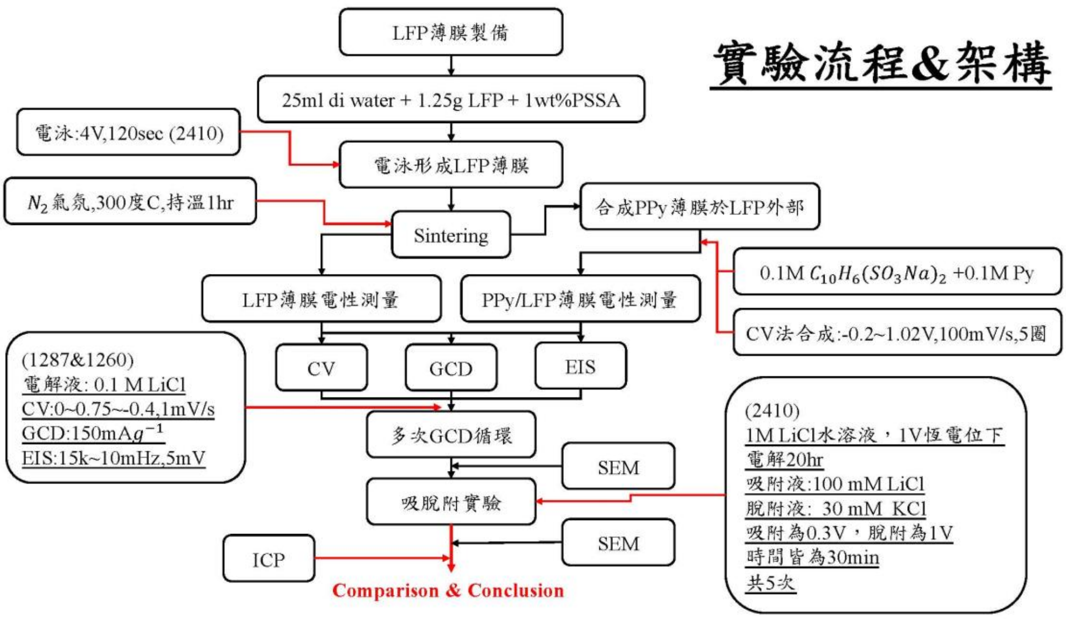
After discharging

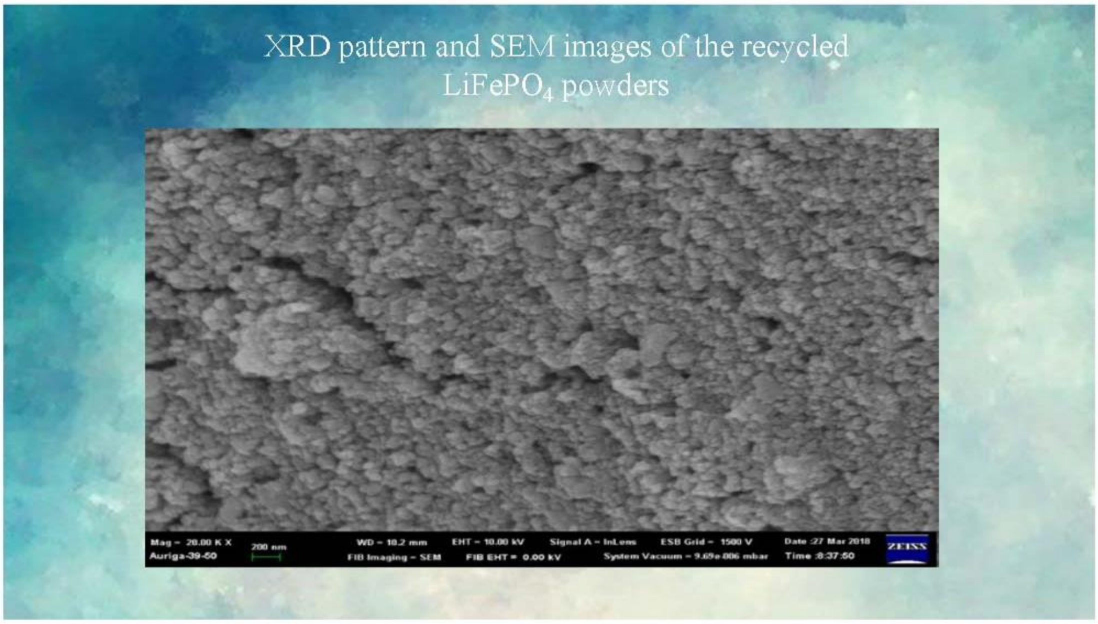
After disassembly

$LiFePO_4$ cathode

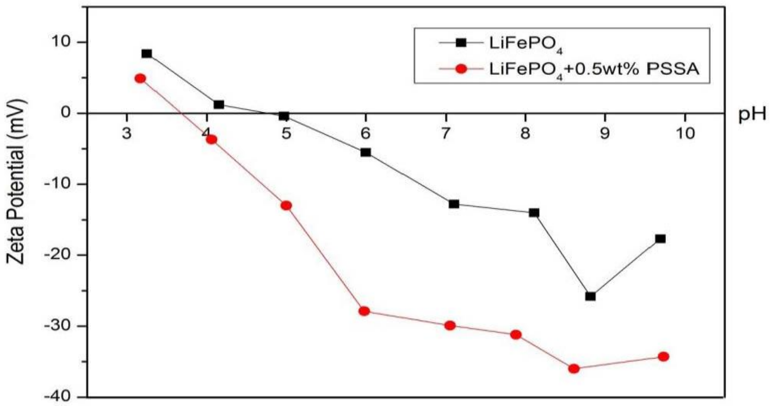
Graphite anode


Recovery process of $LiFePO_4$ powder
01
Leaching cathode in water
Separation from Al foil
02
$LiFePO_4$ washing in DMF
Removal of PVDF and binder
03
Centrifugation-
DMF removal
04
Debinder at 300°C
under N_2

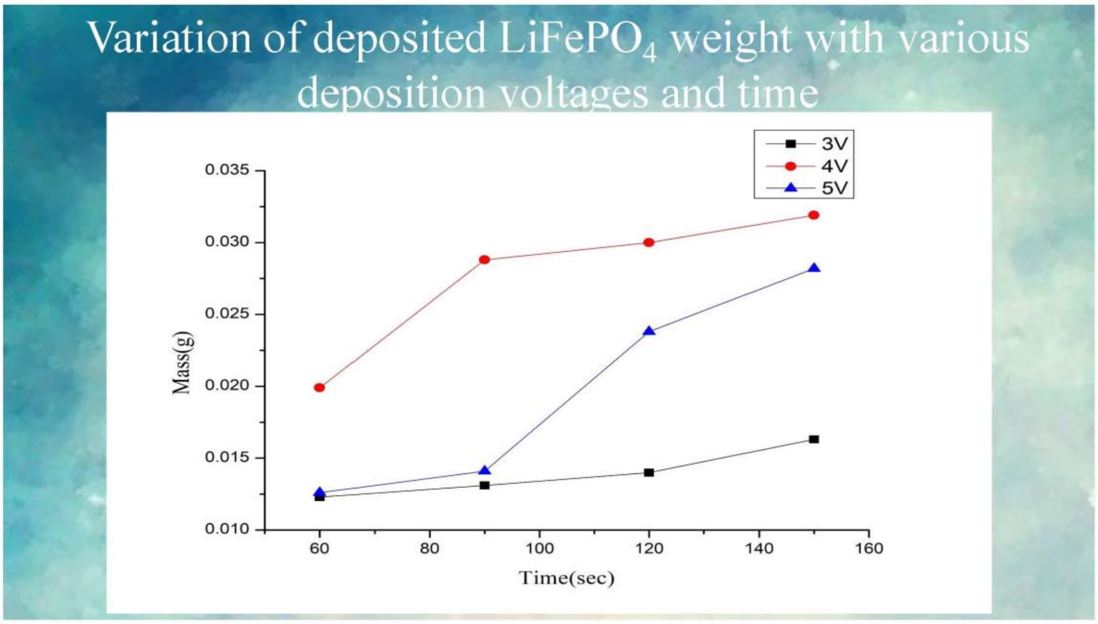

實驗流程&架構
LFP薄膜製備
25ml di water + 1.25g LFP + 1wt%PSSA
電泳:4V,120sec (2410)
電泳形成LFP薄膜
N_2氣氛,300度C,持溫1hr
Sintering
合成PPy薄膜於LFP外部
0.1M $C_{10}H_6(SO_3Na)_2$ +0.1M Py
CV法合成:-0.2~1.02V,100mV/s,5圈
LFP薄膜電性測量
PPy/LFP薄膜電性測量
CV
GCD
EIS
(1287&1260)
電解液: 0.1 M LiCl
CV:0~0.75~-0.4,1mV/s
GCD:150mAg^{-1}
EIS:15k~10mHz,5mV
多次GCD循環
SEM
吸脫附實驗
SEM
ICP
Comparison & Conclusion
(2410)
1M LiCl水溶液，1V恆電位下
電解20hr
吸附液:100 mM LiCl
脫附液: 30 mM KCl
吸附為0.3V，脫附為1V
時間皆為30min
共5次

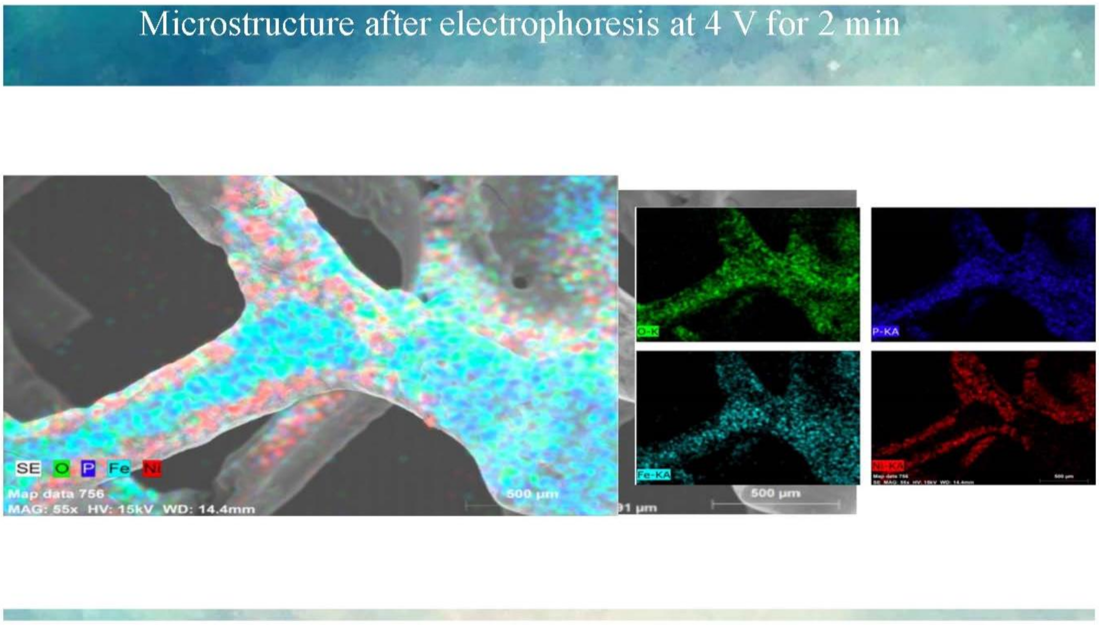


Zeta potential at different pH

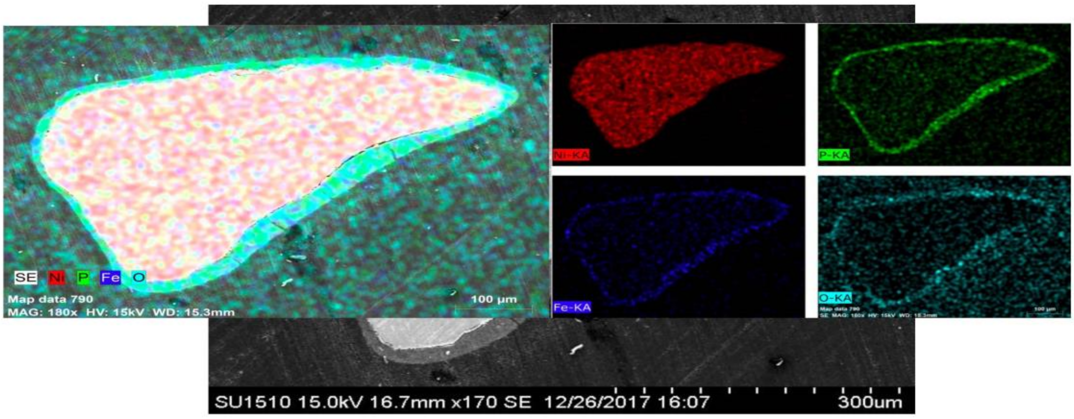


50


Variation of deposited $LiFePO_4$ weight with various deposition voltages and time
3V
4V
5V
Mass(g)
0.035
0.030
0.025
0.020
0.015
0.010
60
80
100
120
140
160
Time(sec)

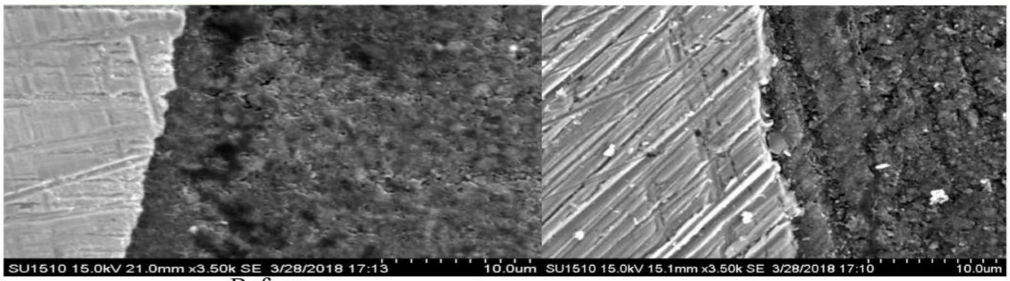

Microstructure after electrophoresis at 4 V for 2 min
SE O P Fe Ni
Map data 756
MAG: 55x HV: 15kV WD: 14.4mm
500 μm
O-K
P-KA
Fe-KA
Ni-KA

Microstructure after electrophoresis at 4 V for 2 min



Effect of heat-treatment on the peeling rate

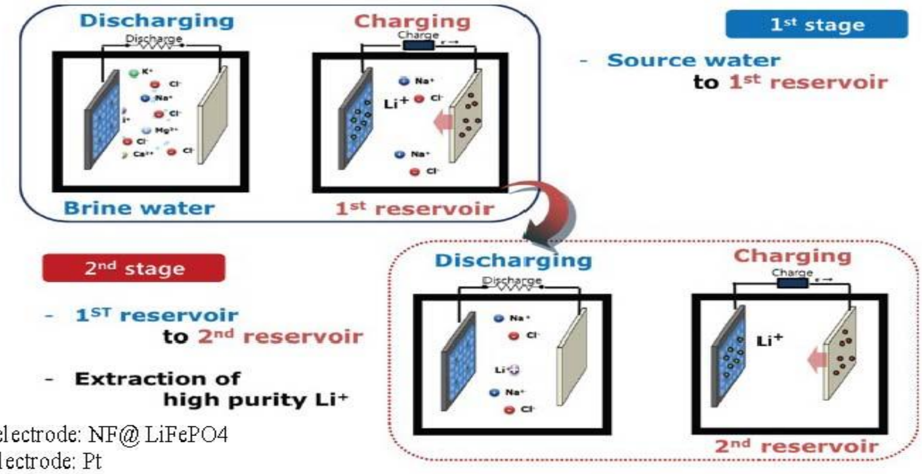
heat-treatment 300°C-1h	Before ultrasonic (g)	After ultrasonic (g)	peeling rate
after	0.5840	0.5830	0.17%
before	0.7773	0.7692	1.04%



Before ultrasonic

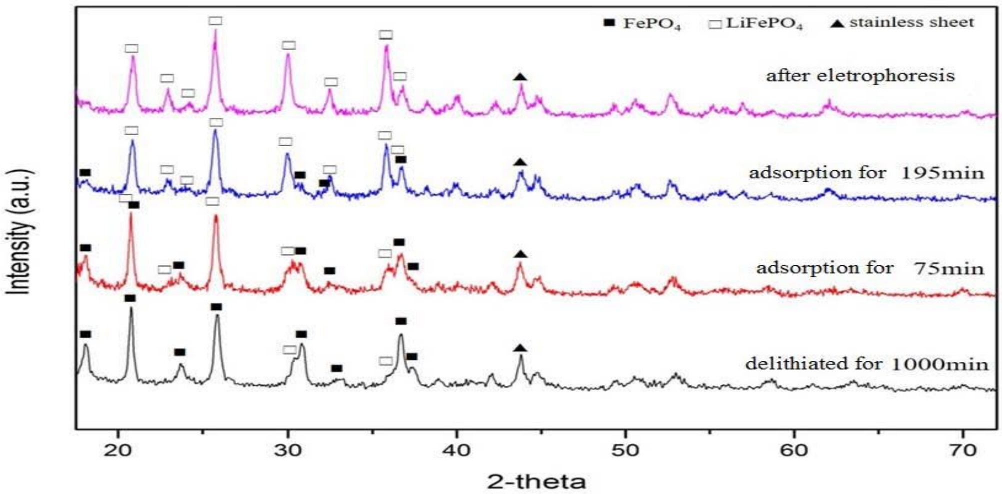
After ultrasonic

Schematic of lithium ion capturing process in simulated brine water



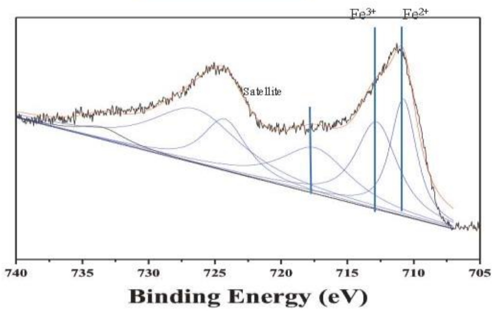
Working electrode: NF@ LiFePO4
Counter electrode: Pt
Working voltage: 0.3-1 V for 10 min.
Cycle times: 1-6

XRD patterns

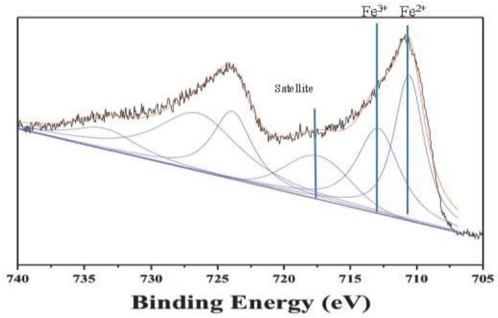


XPS of the sample before and after electro-adesorption

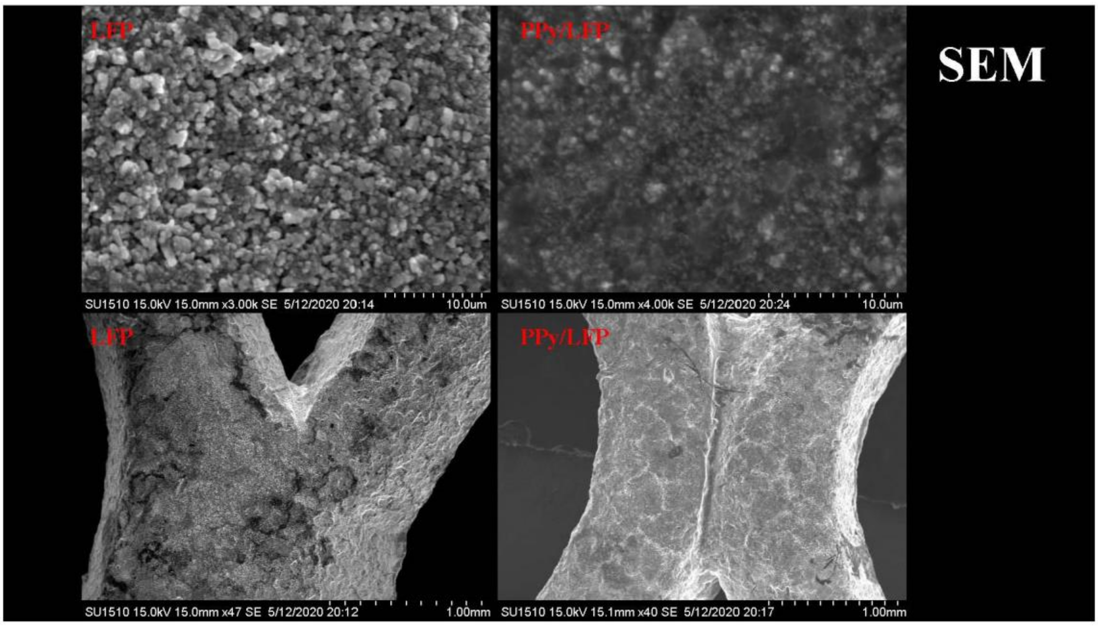
	Fe^{2+}	Fe^{3+}	Fe^{2+}/Fe^{3+}
before	10905.5	12826.11	0.8502
after	15199.03	12562.5	1.2098



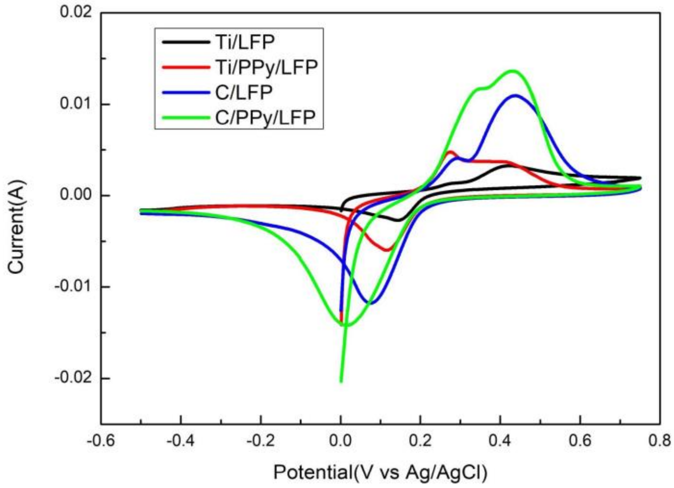
before



after

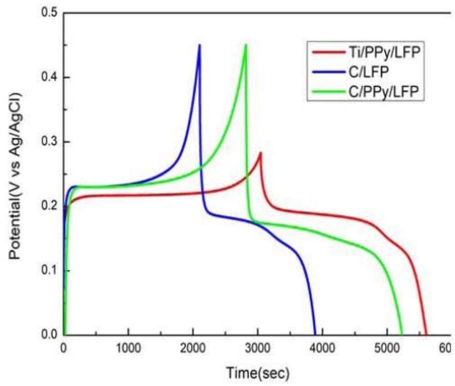


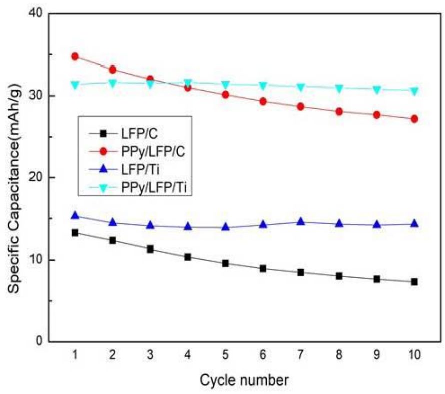
CV



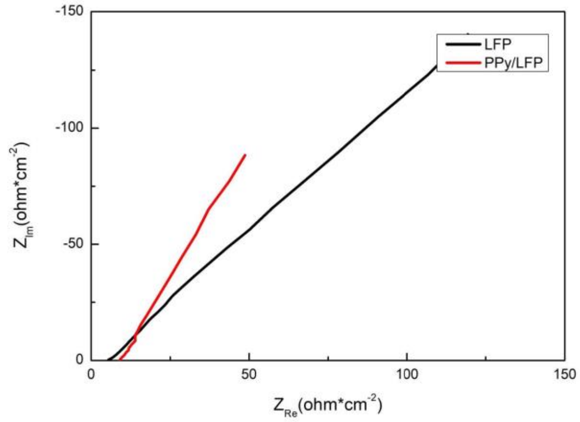
附上PPy得到的CV
峰電流會更高。

GCD





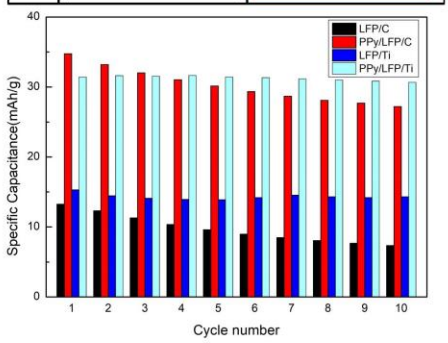
EIS



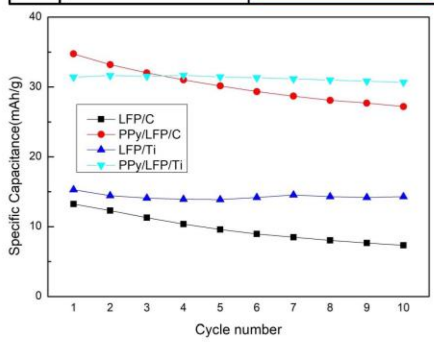
低頻區的斜直線對應離子在固態電極中的擴散阻抗，直線斜率越大表示離子擴散阻抗越小

多次GCD比較

	LFP	PPy/LFP
Ti	平均14.31mAh/g	平均31.26mAh/g
C	平均9.73mAh/g	平均30.2mAh/g

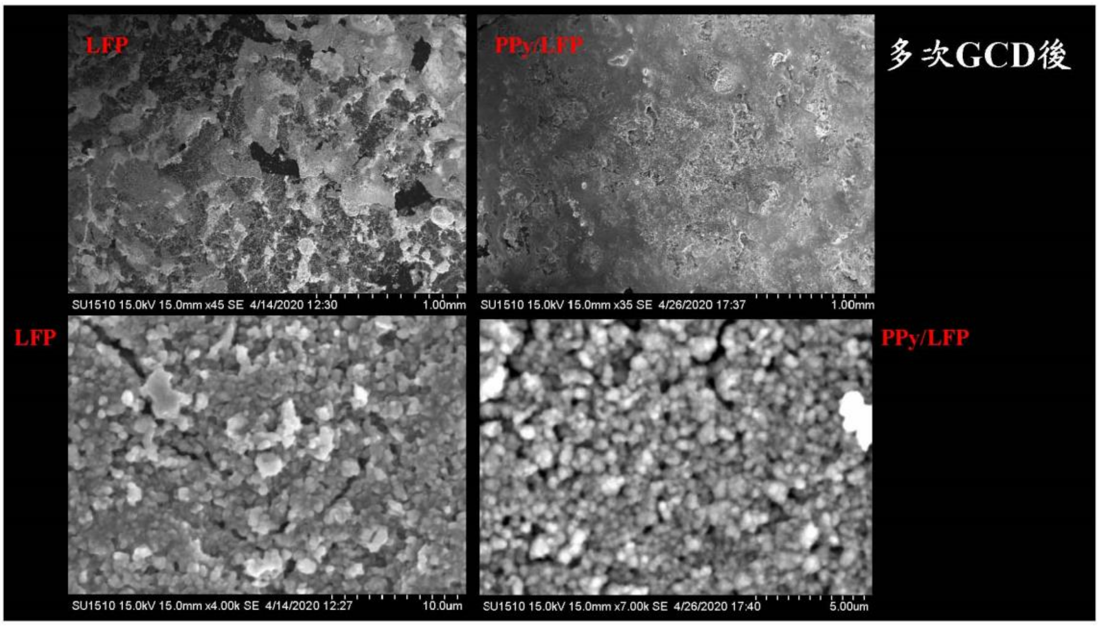


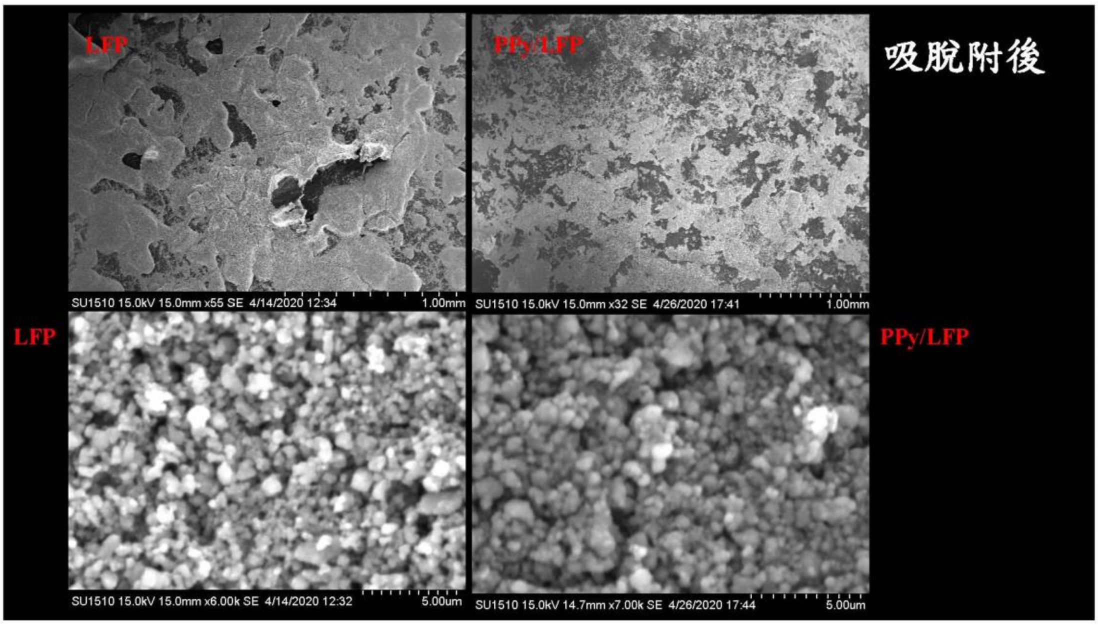
	LFP	PPy/LFP
Ti	在十次循環內仍保持較一致的利用率	在十次循環內仍保持較一致的利用率
C	衰退45%	衰退20%



多次GCD結果

1. PPy薄膜可以提高LFP薄膜的利用率，除了每克LFP電容量提高，也能利用更多LFP。
2. 鈦網為多孔材質，相比碳片，表面積更大，參與反應的LFP更容易觸碰到電解液，因此利用的每克LFP電容量提高，同時也較能維持利用率。
3. 導電高分子PPy+多孔材料鈦網，能賦予鋰離子篩更好的效率。

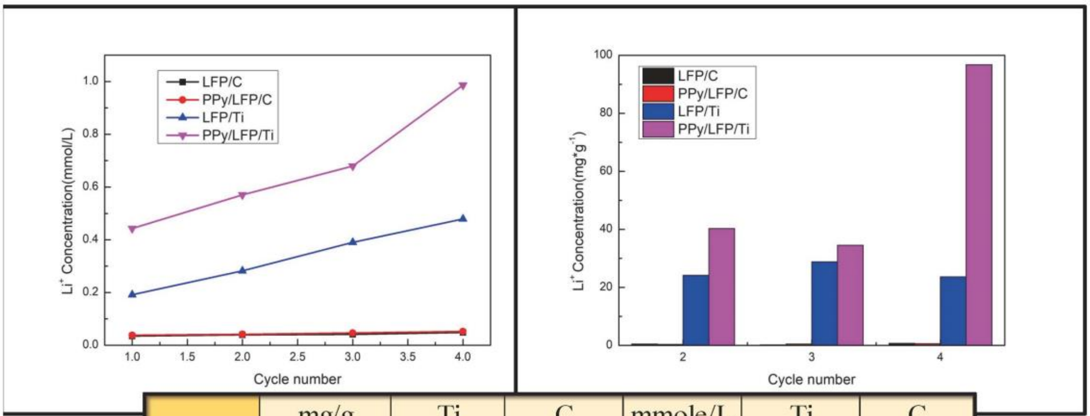




吸脫附實驗

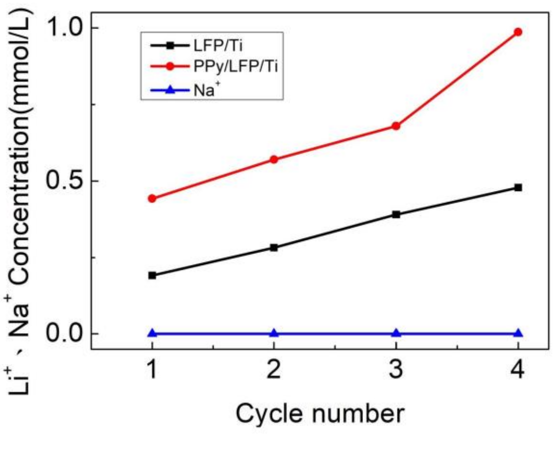
- 吸附液:30mM of each (NaCl, KCl, $CaCl_2$ and $MgCl_2$,LiCl) or 100mM LiCl
- 脫附液:30mM LiCl
- 吸脫附時間:30min
- 吸附電壓:0.3V $e^- + Li+ + FePO4 \rightarrow LiFePO_4$
- 脫附電壓:1.0V $LiFePO_4 \rightarrow Li^+ + FePO4 + e^-$
- 次數:4

Lithium adsorption for different cycles



Ti vs C	mg/g	Ti	C	mmole/L	Ti	C
	LFP	25.5641	0.26	LFP	0.09676	0.036
	PPy	57.1818	0.48	PPy	0.18124	0.05

Ion adsorption selectivity



通過ICP確認Na^+濃度不會改變

證明鋰離子篩吸脫附選擇性

Conclusions

- Two main recovery resources of lithium :
  - Brine water
  - Spent lithium battery
- This lithium recovery system successfully demonstrated that lithium can be selectively recovered from brine water which contains various cations.
- The Li^+ adsorption efficiency of the nanostructured lithium ion sieve and electro-adsorption is better than the traditional ion sieves.
- Novel lithium recovery technology from brine water by using spent $LiFePO_4$ battery was successfully developed.

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Thank you for your attention

EMO電磁光陶瓷實驗室