

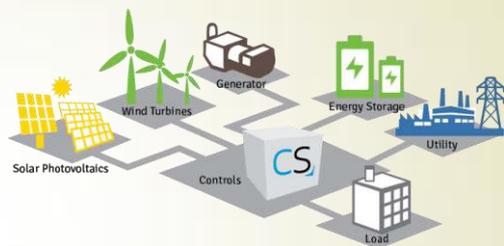
## 充放電技術、綠色能源反應

陳柏端 助理教授  
車輛工程系

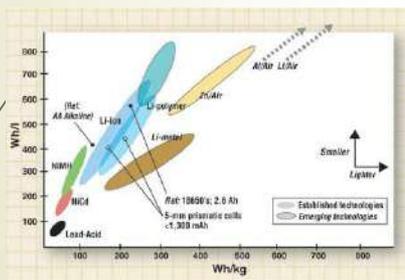


## 綠色能源儲存及電動車

- ▶ 近年來，對於可持續能源及便攜式設備面臨的全球化挑戰，能源儲存技術至關重要
- ▶ 鋰電池是目前發展完善電池之一



用於生活/企業節能



各種電池的比較



用於車輛運輸



The Nobel Prize in chemistry 2019

They developed the world's most powerful battery!!

**惠廷安**  
M. Stanley Whittingham  
78歲，英國、美國籍  
學歷：牛津大學化學博士  
現職：紐約州立大學賓漢頓大學教授

**古德諾**  
John B. Goodenough  
97歲，美國籍  
學歷：芝加哥大學物理學博士  
現職：德州大學奧斯丁分校教授

**吉野彰**  
Akira Yoshino  
71歲，日本籍  
學歷：京都大學工學碩士、大阪大學工學博士  
現職：名城大學教授、旭化成研究員

資料來源：綜合外電

**2019諾貝爾化學獎得主貢獻**  
諾貝爾化學獎得主協力改善發明鋰離子電池，成為今日手機、筆電副電動車所仰賴的能量來源。

1970年代惠廷安發明鋰離子電池，採石墨層結構的硫化鈦為陰極材料，金屬鋰為陽極材料，獲2伏特的高電壓，可重複充電。但金屬鋰在正常環境中易燃，需改進。

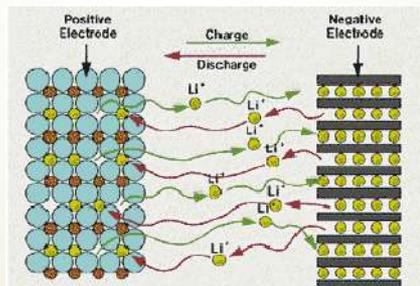
古德諾在1980年代改進鋰離子電池，使用結氧化物製作陰極，可獲更高的4伏特電壓，比先前加倍。

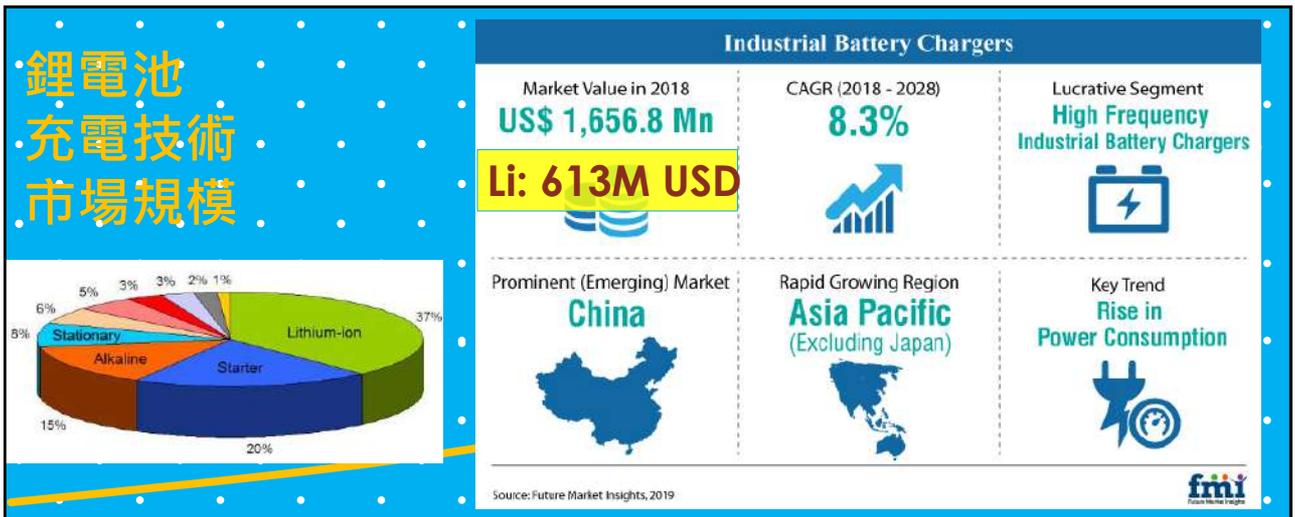
吉野彰改用石油焦製作陰極，使電池免於使用不安定的鋰金屬，1985年成功製作出可商業化應用的鋰離子電池。

資料來源：諾貝爾獎委員會官網

## 鋰離子電池

- 鋰離子電池是一種充電電池，它主要依靠鋰離子在正極和負極之間移動來工作。  
 嵌入：鋰離子進入正極材料，離開為脫嵌。  
 插入：鋰離子進入負極材料，離開為脫插。
- 易與下列兩種電池混淆：鋰電池：存在鋰單質。鋰離子聚合物電池：用多聚物取代液態有機溶劑。





- 1**  
充電電池的市場中  
鋰電池佔比 **37%**.
- 2**  
鋰電池充電市場規模：  
**61.3億美  
元**
- 3**  
年複合成長率：  
**8.3%**
- 4**  
亞洲為快速成長的市場，特別是  
**中國大陸**

## 市場痛點

使用充電電池的同時，  
電池壽命便漸漸....  
消逝！！

充電時間很久？

充飽電，很快就沒電???

電池爆炸的恐懼！

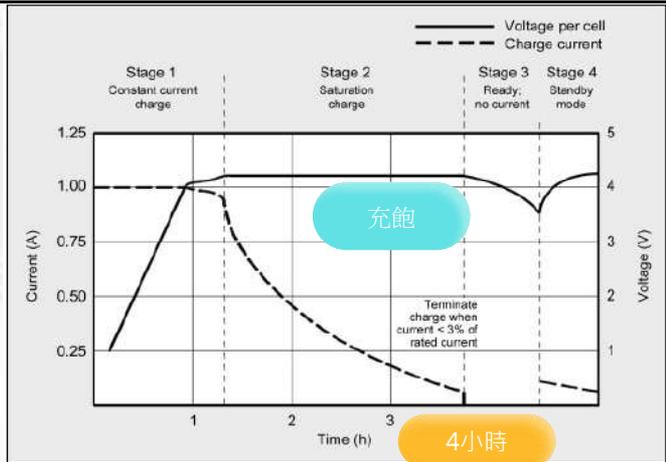
昂貴的電池維修費用，值得嗎？

# 冗長的 充電時間 而忘記拔掉 插頭？



充電要等很久，就放著讓它慢慢充電吧....

過度的充電讓你置身於電池的爆炸危險中！！



充電時間

理論上，需要四小時才能完整充電一顆18650鋰電池。

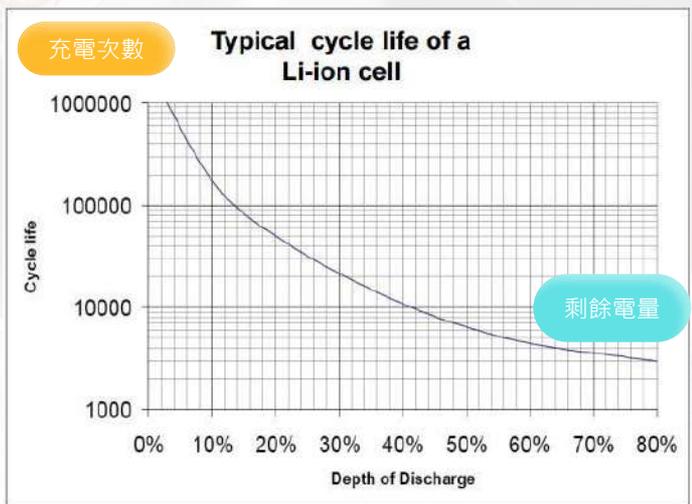
電量

電量隨著充電次數增加而減少。

# 越常使用 壽命越短？



鋰電池最為人詬病的問題就是一開始使用，便注定壽命不斷降低！



充電循環次數

電池壽命隨著使用次數便快速下降！

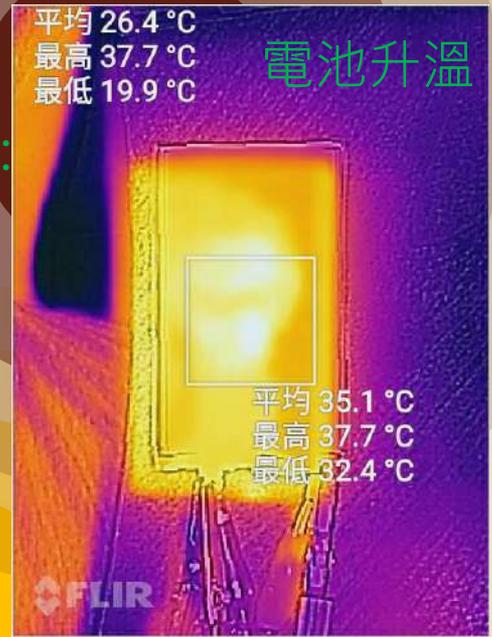
剩餘電量

理想狀態下，3000次充放電循環後，電量只剩80%。

# 產業痛點

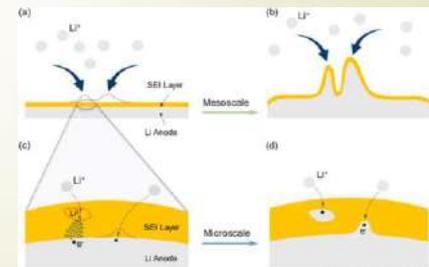
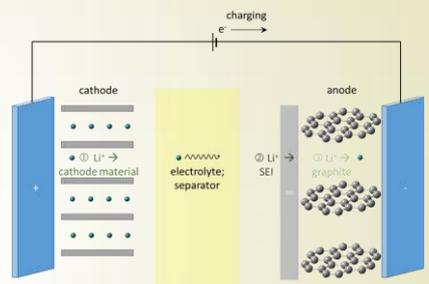
輕薄的設計需求所面臨到的問題：

電池膨脹



Issue:

**Overcharging** may lead to Li stack on negative electrode. The formation of **Li dendrite** results in serious safety problem.

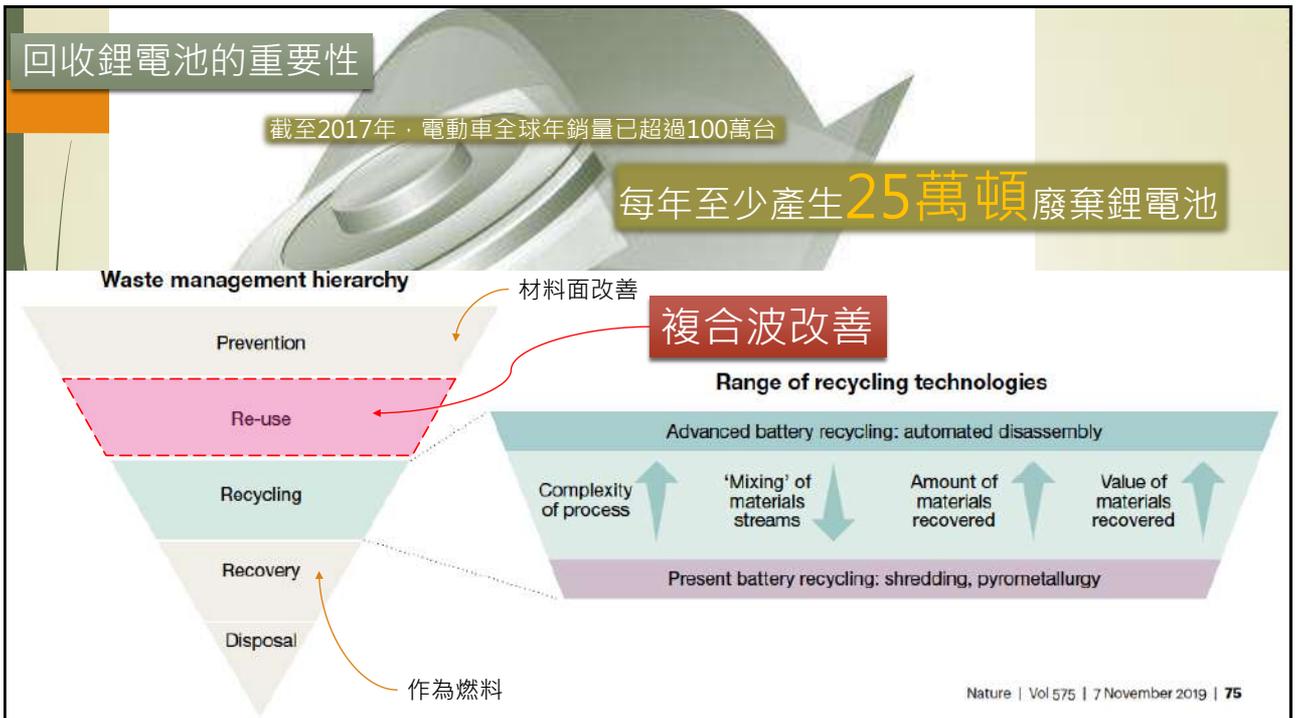
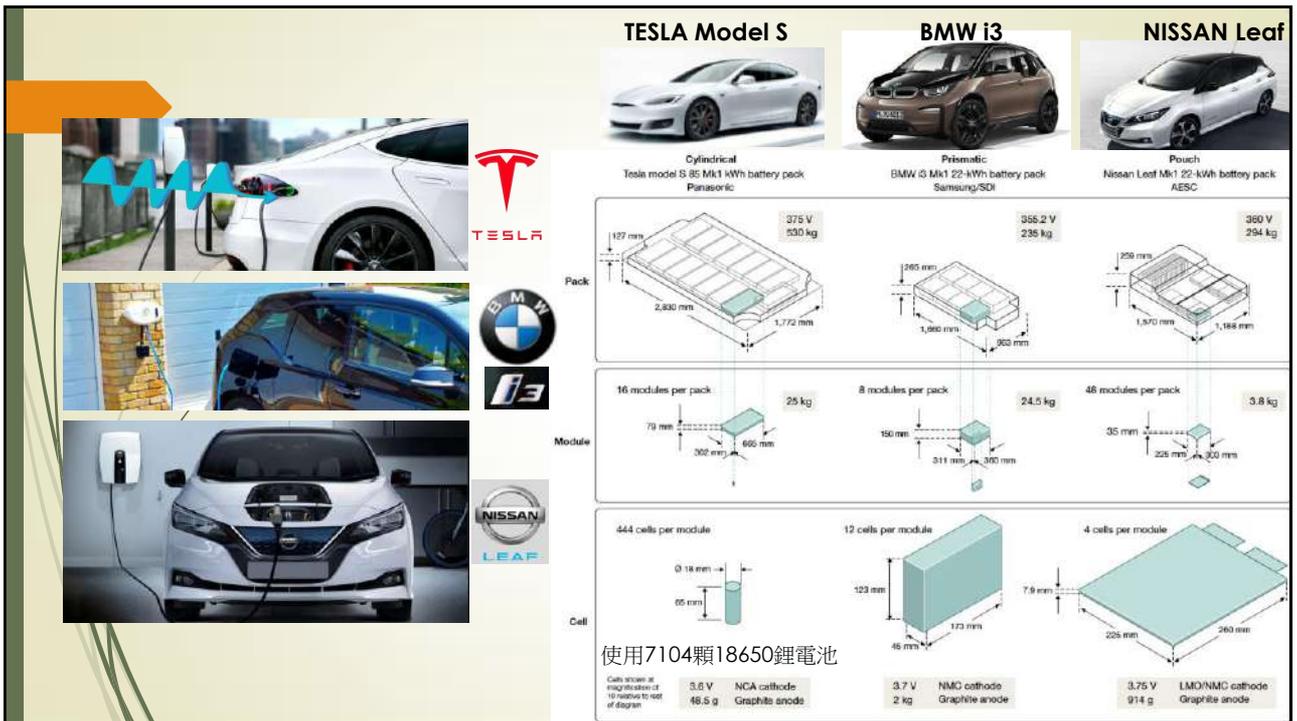




# 18650 鋰電池- 世上最被廣泛使用的鋰電池

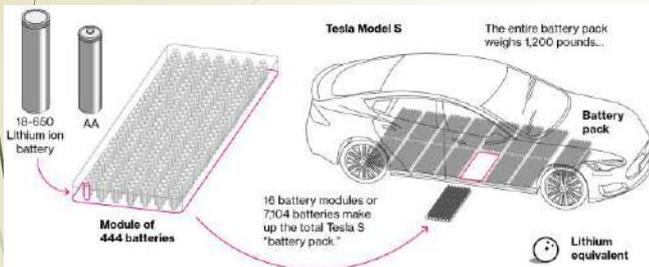
18650 鋰電池的使用已深入你我的生活中

- 行動電源
- 電動機車電池
- 各種電動工具
- 各式家電
- 電動汽車電池
- 各式電器



## 電池老化造成的工業問題

範例：



特斯拉顧客最主要考量的議題：  
電池的循環壽命如何？

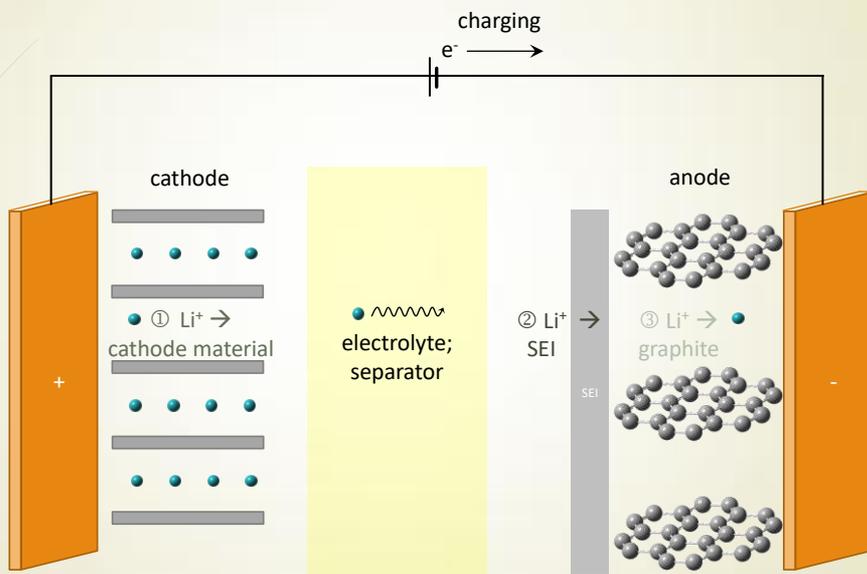
蘋果電池門事件：iOS軟體讓舊型iPhone效能降低，造成全球大量果粉的不滿

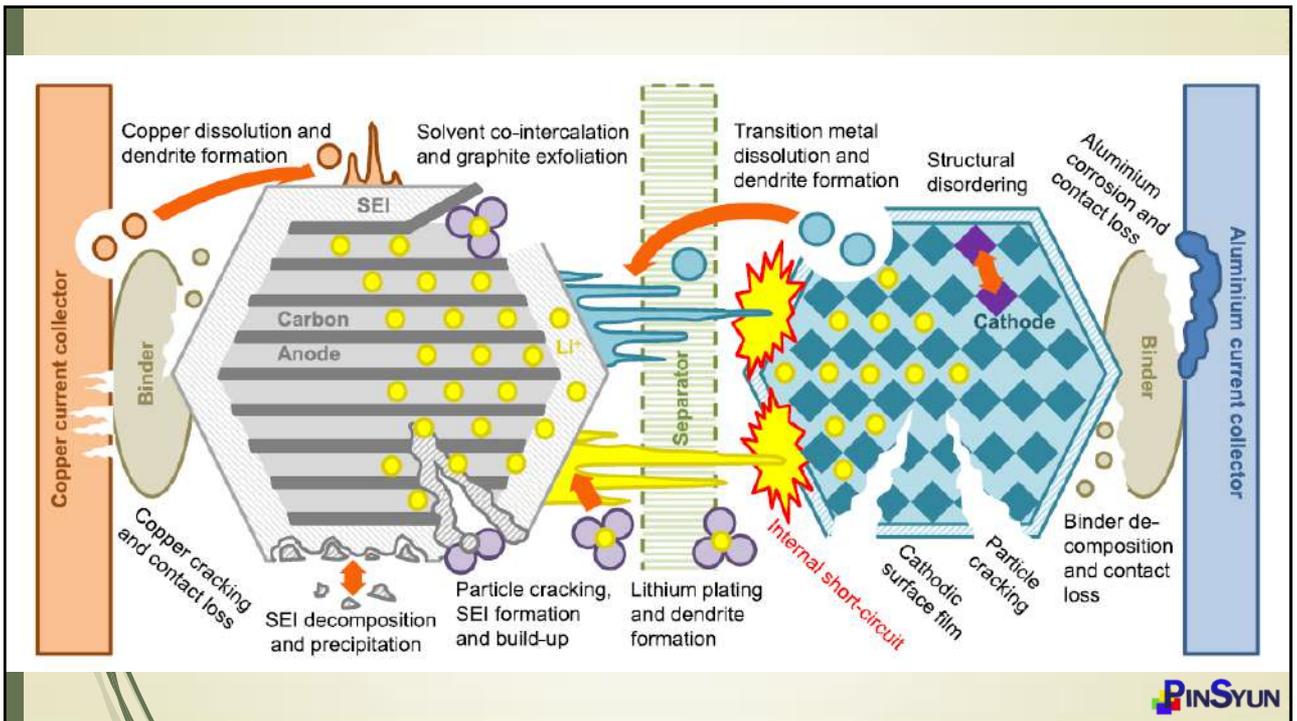


避免電池老化的可行方案：  
有些學者認為適當的充電策略可能延長電池循環壽命



## 充電引起電池老化





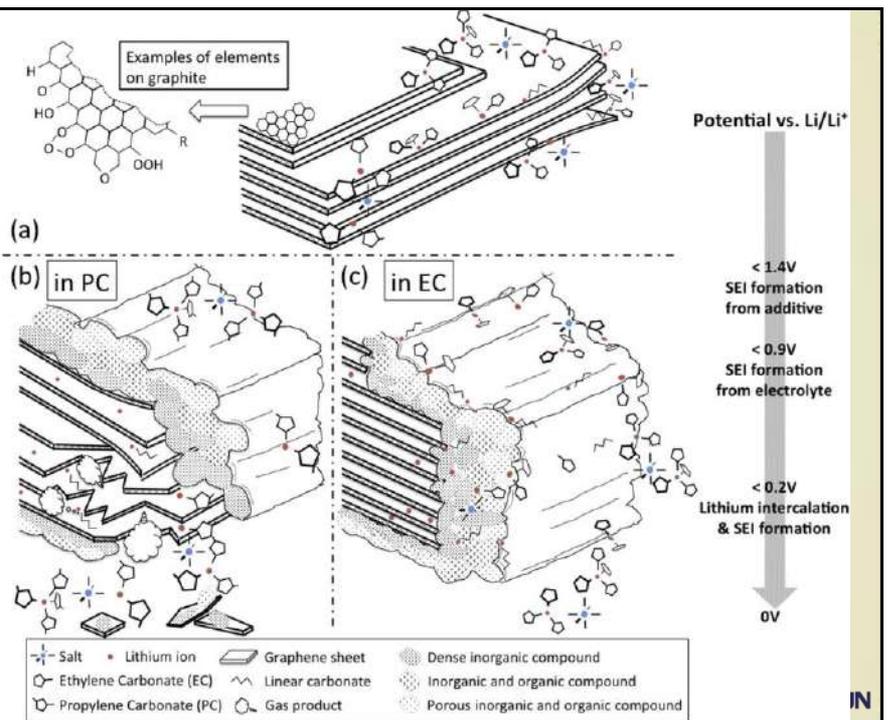
### 固體電解質介面膜 (SEI) 形成

固體電解質界面膜 (SEI) · 產生在電極材料和電解質的界面

SEI主要的目的是為了保護電極

然而 · 在充電/放電過程中持續產生的SEI · 卻是鋰電池主要的老化方式

An et al, Carbon 105 (2016) 52-76.





**充電方式**

**恆定電壓**

- 向電池**持續注入能量**會造成**有害化學反應**，進而**損害電池**
- 在化學品充電過程中，留下靜置時間可能是必須的

**脈衝充電**

- 在脈衝充電過程中，脈衝間的**短暫靜置時間**使化學作用趨於穩定
- 這使化學反應能夠跟上電能輸入的速度

**反向脈衝充電**

- ◆ 在充電靜置期間施加非常短的放電脈衝
- ◆ 反向脈衝充電方式應該可**減少不必要的化學反應**

PINSYUN

**OPPO 110W 超閃餅乾充電器**在全行業首創脈衝充電，將交流電直接轉化為100Hz的脈衝直流電，以10ms為一周期穩定波動，最高電流為5.5A。

該技術的優勢在於可在停充期間消除電池的濃差極化和歐姆極化，進而有效保證充電速度與充電穩定性，減少發熱，進而延長電池壽命，所以可以採用較大電流充電

原文網址：<https://kknews.cc/digital/a6g439n.html>

PINSYUN

### THE reFLEX PRINCIPLE OF CHARGING NICKEL-CADMIUM AND OTHER BATTERIES

Fred Benjamin

Christie Electric Corp., Los Angeles, California

NOTE: This paper was presented at the IEEE Power Processing and Electronics Specialists Conference held at Atlantic City, N.J., on May 22, 1972, in conjunction with the 25th Power Sources Symposium sponsored by the United States Army Electronics Command. Additional reprints available from Christie Electric Corp., P.O. Box 60020, Los Angeles, California 90060.

PPESC 72 RECORD — 111

#### Different Kind of Fast Charger

The reFLEX charger is a fast charger. But in the past this has been primarily associated with units which bring a dead battery at a gas station up to partial charge within 30 to 45 minutes (Fig. 5). With car batteries this is sufficient since the charge will be completed leisurely by the car generator or alternator while driving afterwards. Partial charging otherwise results in a permanent degradation of the battery.



Fig. 5 Automotive Charger

The reFLEX charger was introduced in 1969 as part of a third generation Charger/Analyzer for ground maintenance of aircraft batteries. Previous units employed constant potential and two-rate constant current, respectively. Since that time, reFLEX chargers have won widespread acceptance by airlines, business aircraft owners, branches of the Army, Air Force, Navy and NASA, as well as other nickel-cadmium battery users.



Fig. 10 reFLEX Charger/Analyzer



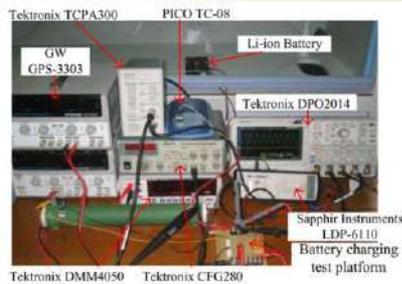
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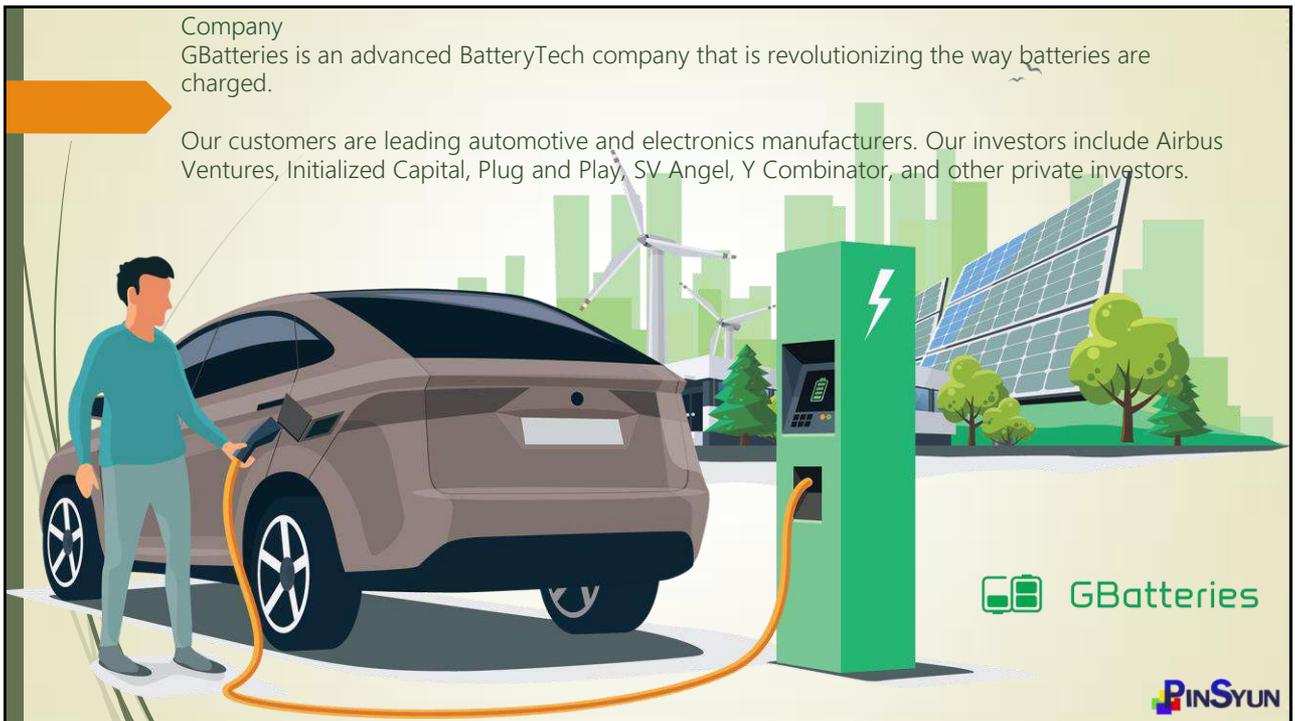
IEEE TRANSACTIONS ON INDUSTRIAL ELECTRONICS, VOL. 60, NO. 1, JANUARY 2013

## Sinusoidal-Ripple-Current Charging Strategy and Optimal Charging Frequency Study for Li-Ion Batteries

Liang-Rui Chen, Member, IEEE, Shing-Lih Wu, Student Member, IEEE, Deng-Tswen Shieh, and Tsair-Rong Chen

Abstract—In this paper, the sinusoidal-ripple-current (SRC) charging strategy for a Li-ion battery is proposed. The ac-impedance analysis is used to explore the optimal charging frequency. Experiments indicate that the optimal charging performance can be achieved by the proposed SRC with the minimum-ac-impedance frequency  $f_{Z_{min}}$ . Compared with the conventional constant-current constant-voltage charging strategy, the charging time, the charging efficiency, the maximum rising temperature, and the lifetime of the Li-ion battery are improved by about 17%, 1.9%, 45.8%, and 16.1%, respectively.





Company  
GBatteries is an advanced BatteryTech company that is revolutionizing the way batteries are charged.

Our customers are leading automotive and electronics manufacturers. Our investors include Airbus Ventures, Initialized Capital, Plug and Play, SV Angel, Y Combinator, and other private investors.

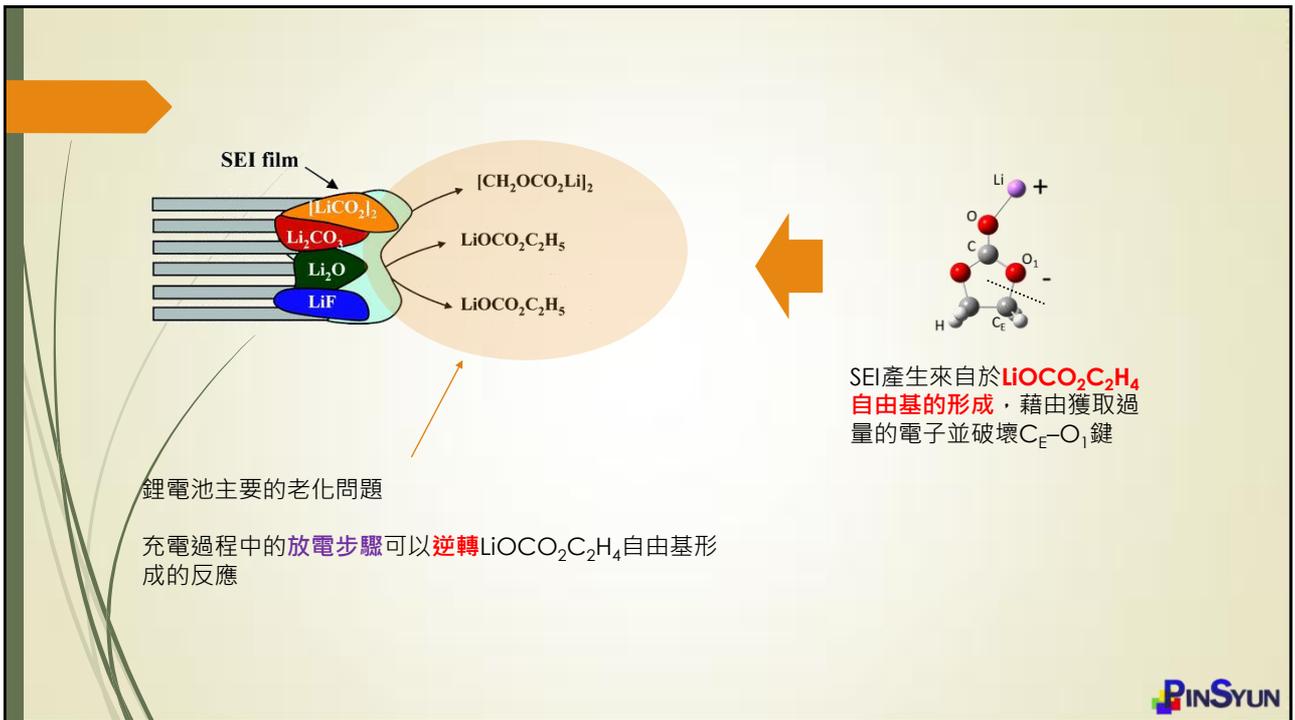
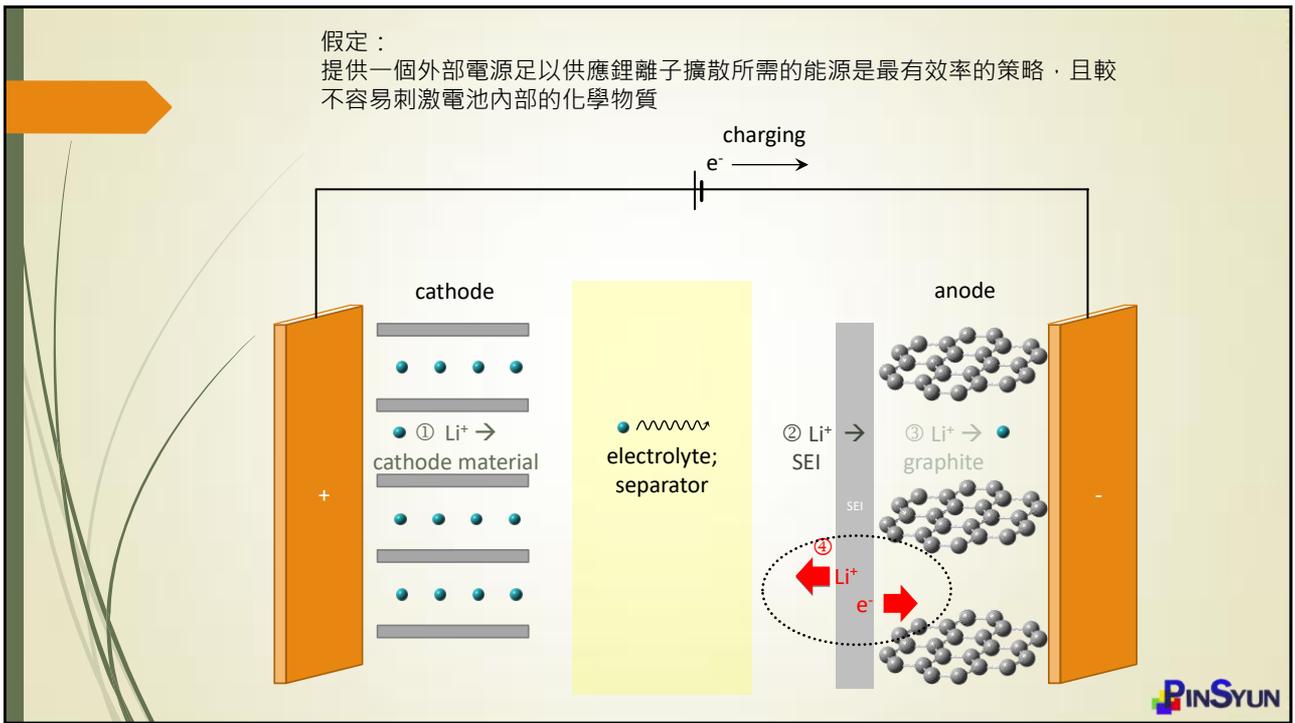
 GBatteries



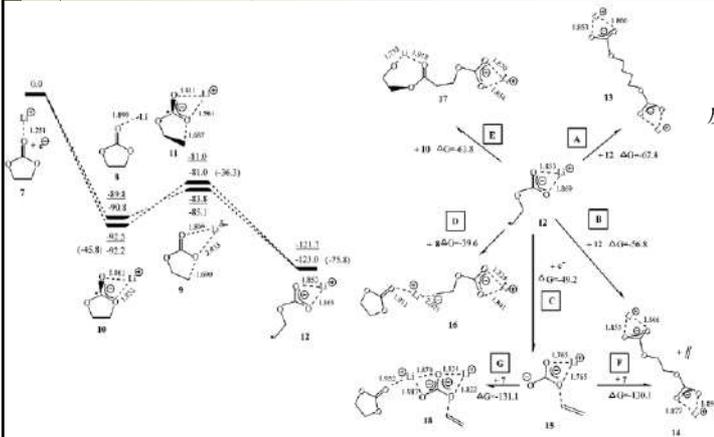


*Why reFLEX ???*

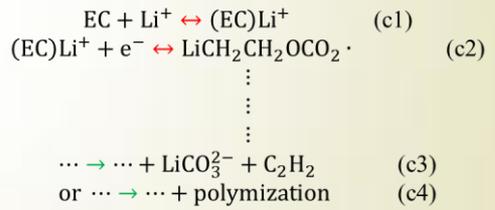




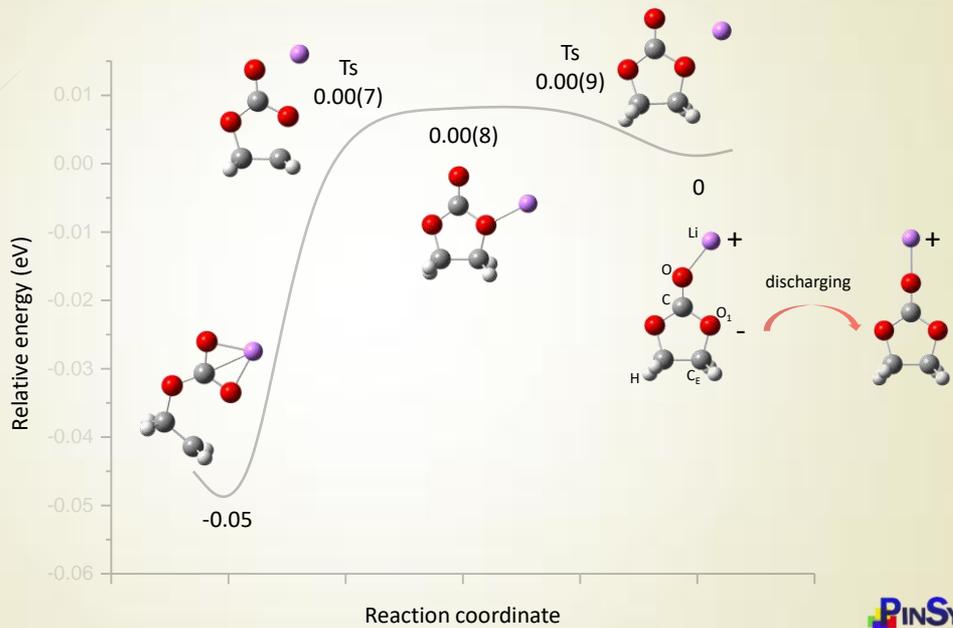
## SEI 形成



普遍認為方程(c3)和方程(c4)的電池老化是不可逆的反應，但方程(c1)和方程(c2)可以是可逆的反應



## 逆轉EC還原反應

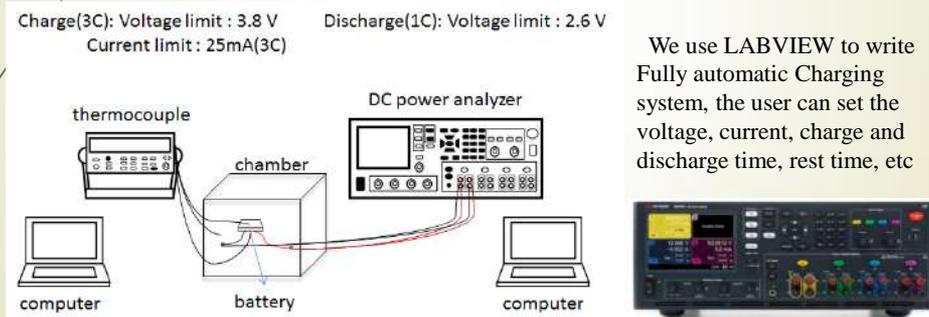


**Based on the above,**  
**we design the charging parameters**  
**of reFLEX charging**



**Generate the reFLEX charging waveform**

In order to make the experiment more accurate, we imported a commercial instrument Keysight N6705C DC Power Analyzer, and added computers, equipments and added an automated program to precisely control the reFLEX charging.





PERGAMON

Electrochimica Acta 47 (2002) 1217–1223



ELECTROCHIMICA  
Acta

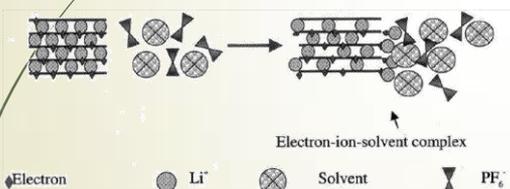
www.elsevier.com/locate/eleacta



TAIPEI 國立臺北科技大學  
TECH National Taipei University of Technology

### Mechanism of self-discharge in graphite–lithium anode

Rachid Yazami <sup>\*1</sup>, Yvan F. Reynier  
*LEPMI INPG/CNRS 5631-BP75, 38402 Saint Martin D'Hères, France*



Electron-ion-solvent complex

Fig. 10. Schematic representation of the mechanism of the electron-ion-solvent complex formation.

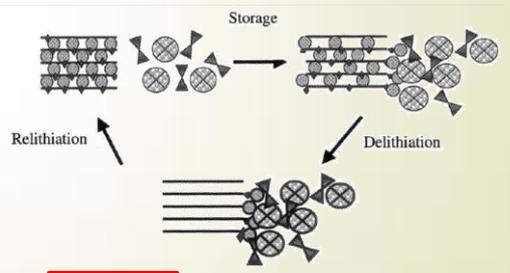
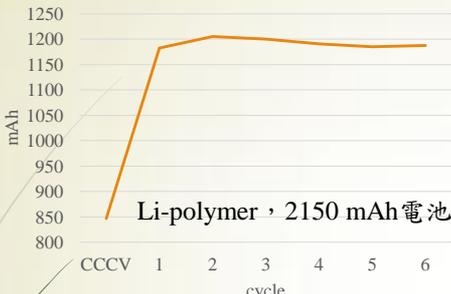


Fig. 11. Reversible capacity loss: the electron-ion-electrolyte complex dissociates to its elements.

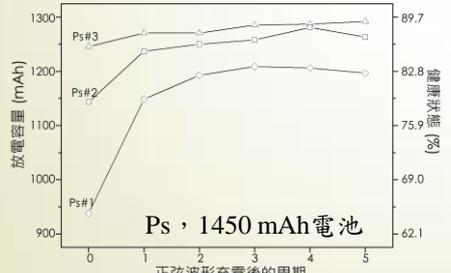




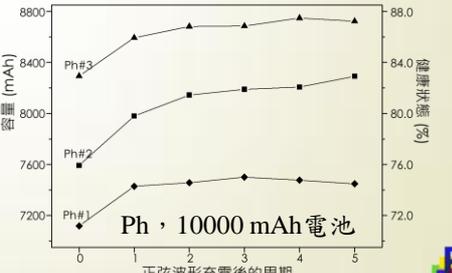
Li-polymer, 2150 mAh電池

使用軟包鋰聚合物電池(iPhone電池)，可多充約20%電量。

新頭殼newtalk | 張嘉哲 綜合報導發布 2019.01.15 | iPhone「電池門」事件虧大了！蘋果去年共換掉1100萬顆電池



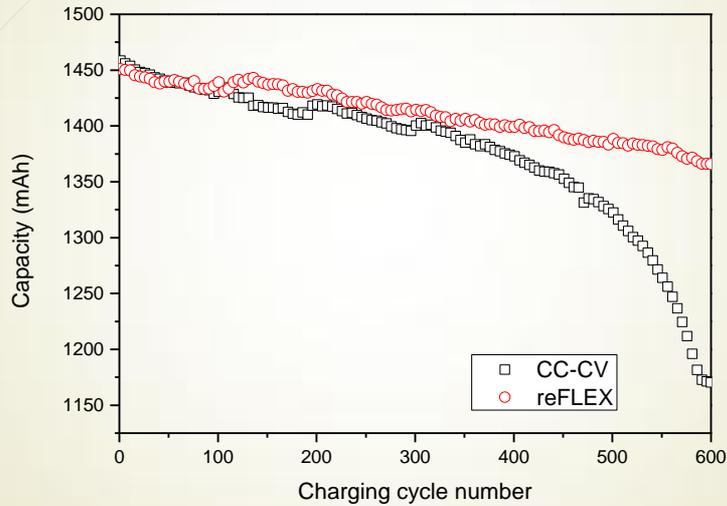
Ps, 1450 mAh電池



Ph, 10000 mAh電池

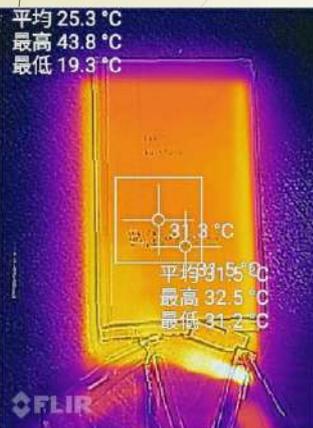


## 延長循環壽命

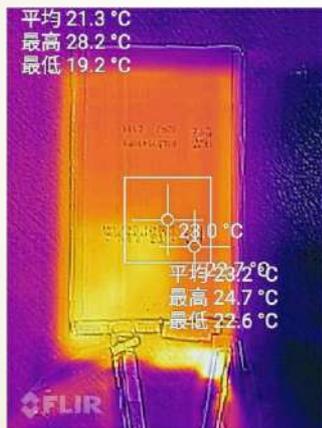


## 抑制溫度上昇

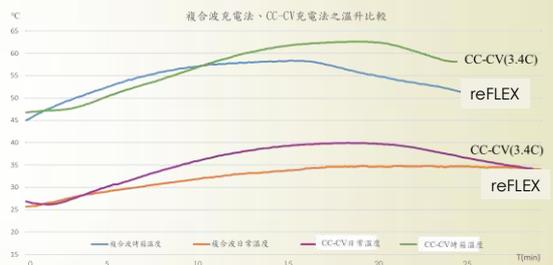
CCCV



reFLEX



充電溫度差異達10°C



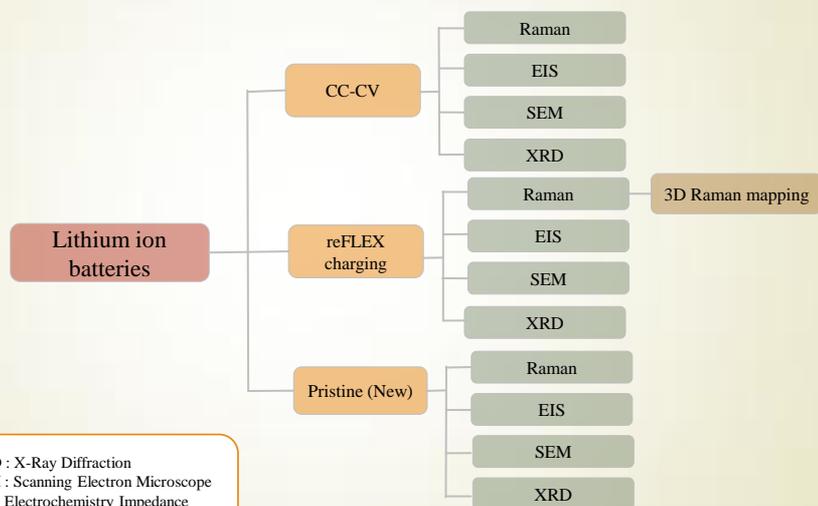
複合波充電法與CC-CV充電法比較，其中CC-CV所用電流為5A(3.4C)。由圖看出，現今普遍使用的CC-CV充電法，其充電升溫都高於reFLEX充電法。



# Still a hypothesis



## Characterization of the reFLEX effect



## Charging-discharging cycles





Remove outside film → Take off the PCBA → Use battery cells to do experiment

thermocouple  
chamber  
DC power analyzer  
battery  
computer

Put the battery cell into the chamber and connect the wires, including the positive and negative electrodes, and the temperature test wire, set the computer up, and start the charging-discharging.

## Battery disassembly

Remove the battery packaging film

Vacuum the glove box and set it to a safe environmental

Put the soft pack battery in the glove box

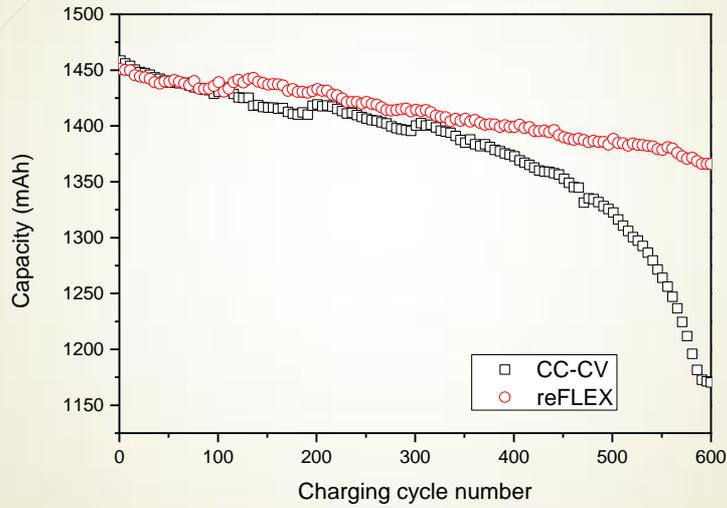
Start to disassemble the battery and separate its positive electrode, negative electrode and separator



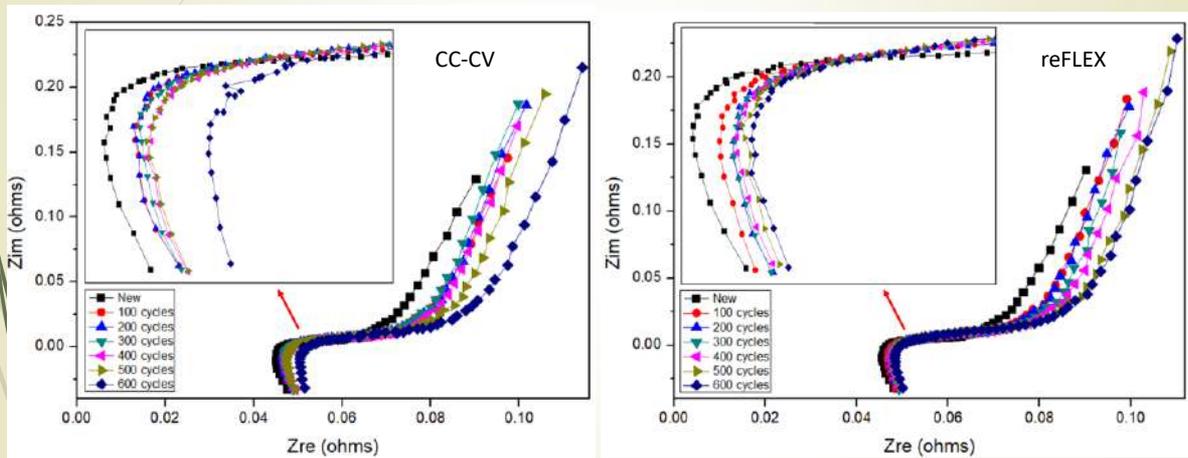

cut

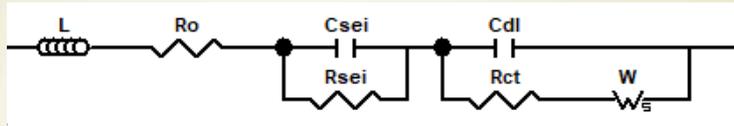


### 表徵複合波的影響



### 無損測量-電化學阻抗譜





reFLEX							
	New	100	200	300	400	500	600
$R_{\Omega}$ (m $\Omega$ )	45.66	46.89	47.59	47.59	47.72	48.05	48.38
$R_{SEI}$ (m $\Omega$ )	3.63	3.51	3.48	3.55	3.62	3.64	3.71
$R_{CT}$ (m $\Omega$ )	5.30	6.44	6.61	6.99	7.05	7.36	7.62
CC-CV							
	New	100	200	300	400	500	600
$R_{\Omega}$ (m $\Omega$ )	45.11	46.71	46.61	46.99	47.46	47.50	50.50
$R_{SEI}$ (m $\Omega$ )	3.31	3.91	3.49	3.56	3.67	3.81	4.25
$R_{CT}$ (m $\Omega$ )	4.77	6.81	6.35	6.53	7.44	7.51	7.93



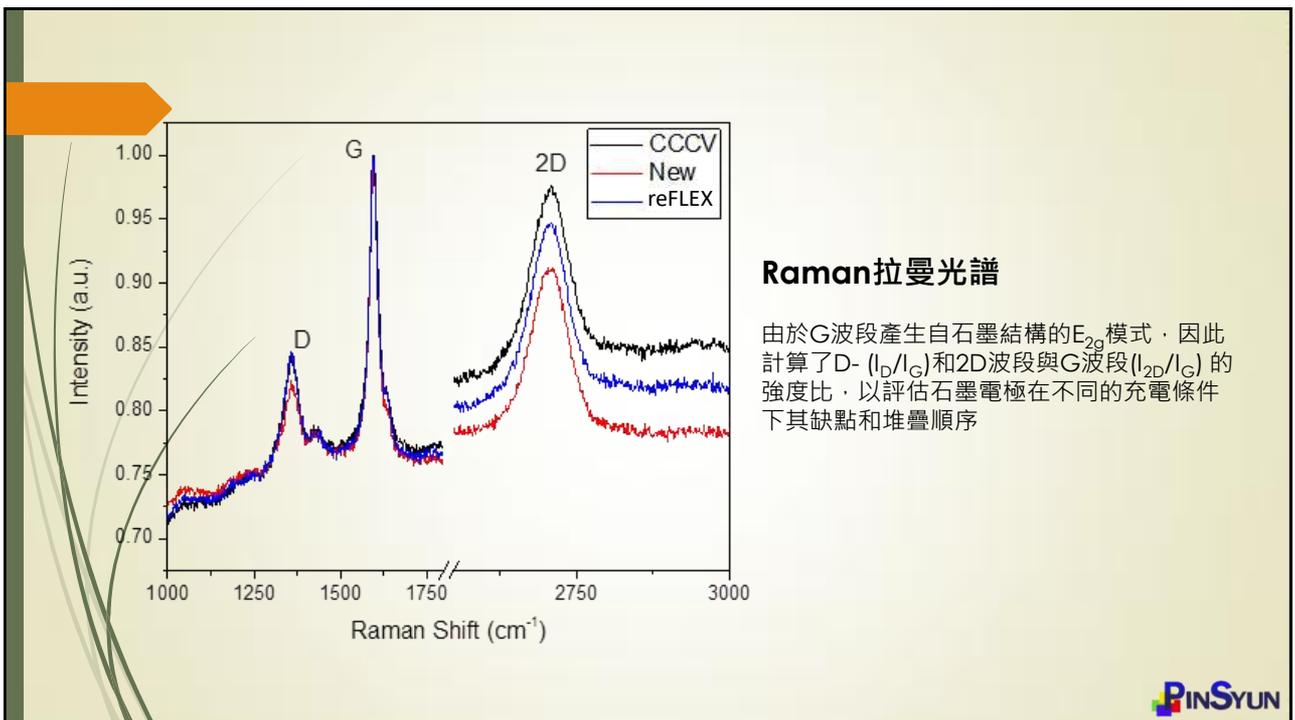
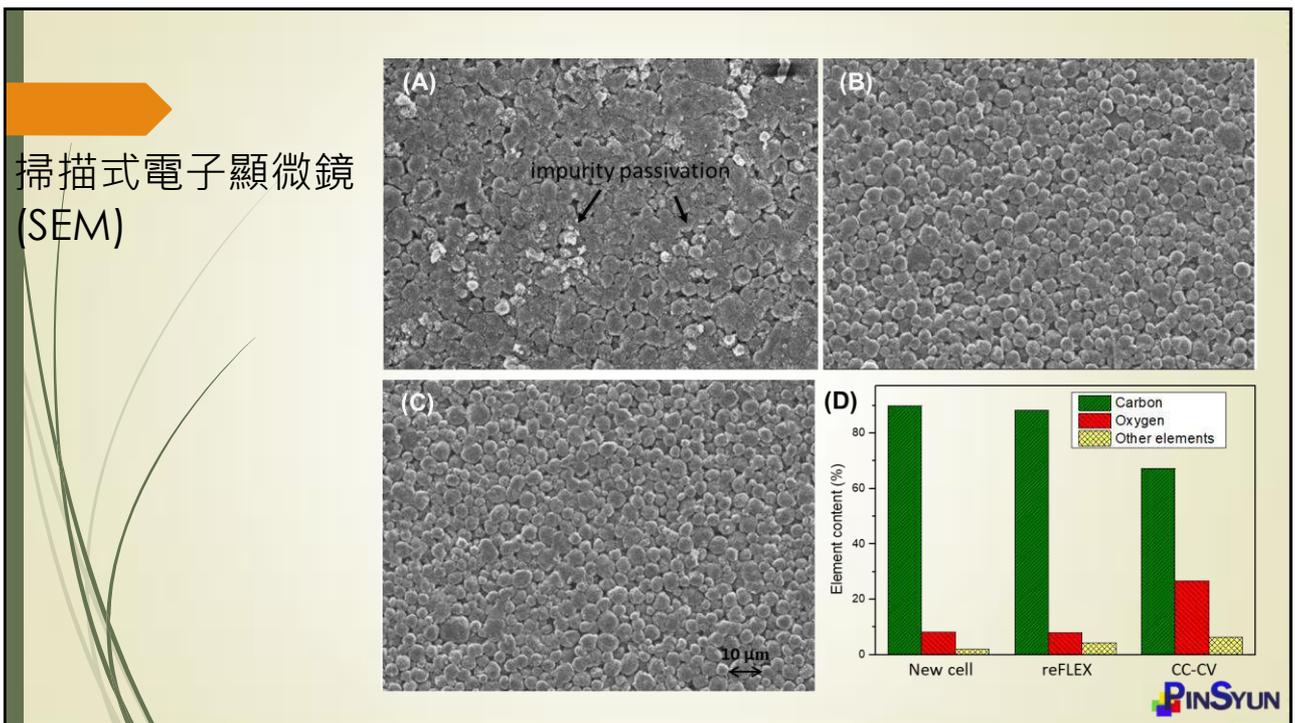
## 損壞的電池及相片

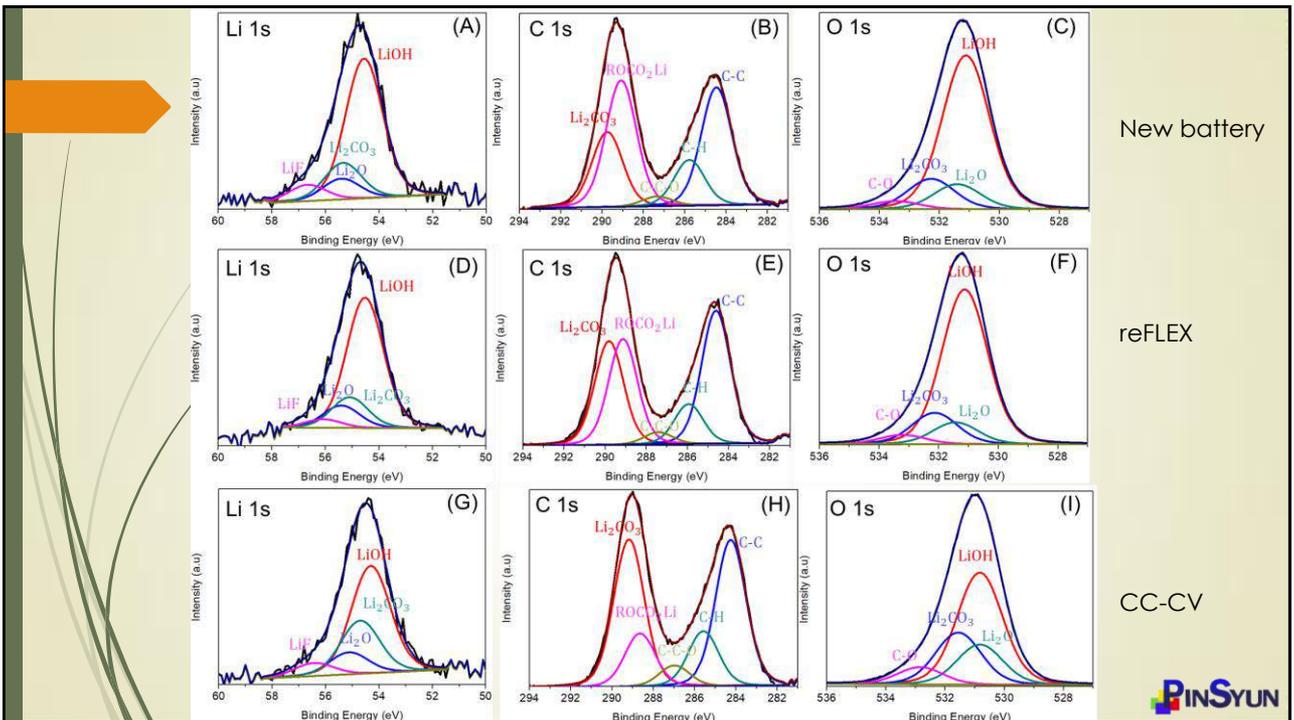
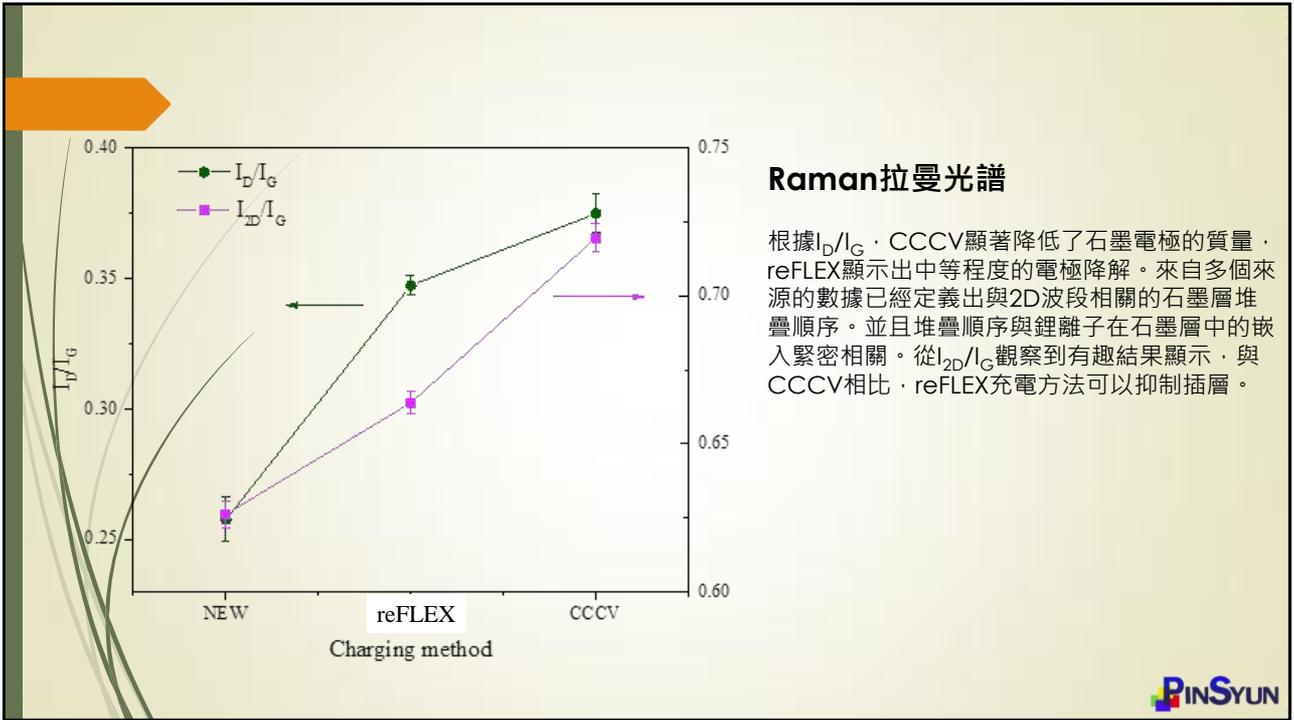


reFLEX

CC-CV







## 小結

- ▶ 調節充電過程中鋰離子的能量是由DFT計算決定。
- ▶ 調節的能量來源可以是外部的電源。
- ▶ 使用這種充電策略是**非常簡單且低成本**的方式，可以讓：
  - 鋰離子電池恢復活力；
  - 延長循環壽命；
  - 降低內部阻抗；
  - 降低電池溫度



利用原位衰減式全反射傅立葉轉換紅外光譜監控反向脈衝充電法對鋰電池固體電解質介面層生成之抑制

**Monitoring the suppression of SEI generation in lithium batteries by using reFLEX charging method with in-situ ATR-FTIR**



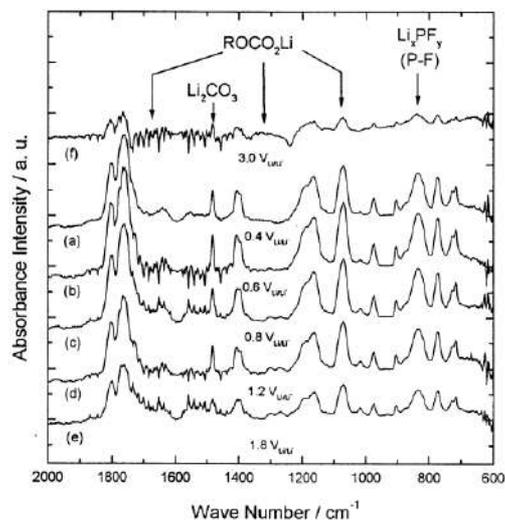
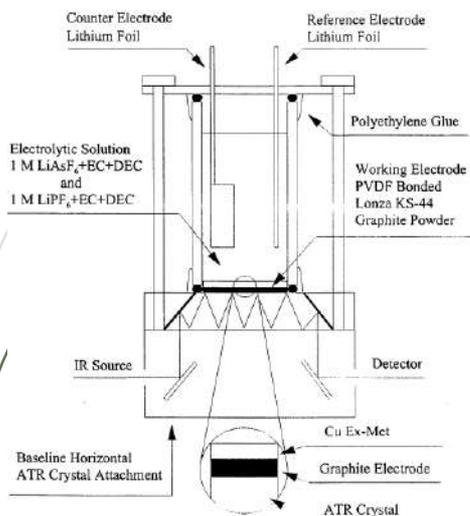
## 常見SEI研究方法

SEI膜因為只有10~100 nm，又十分容易受大氣氣體等汙染影響其性質和組成，針對探討因素選擇適量測手法。常見研究方法有電化學法、譜學法及顯微法。

將上述SEI膜研究方法分類的話，主要可以分為以下幾項：

1. 提供較**準確**SEI膜定性的方法：**FTIR**、Raman、XPS、XRD、SIMS；  
較不能提供準確SEI膜定性的方法：顯微法、EDAX、NMR。
2. 會對電極表面造成破壞或影響SEI膜組成的方法：XPS、SIMS；  
對電極表面**破壞極影響較少**的方法：**FTIR**、Raman。

## 負極材料SEI in-situ FTIR研究

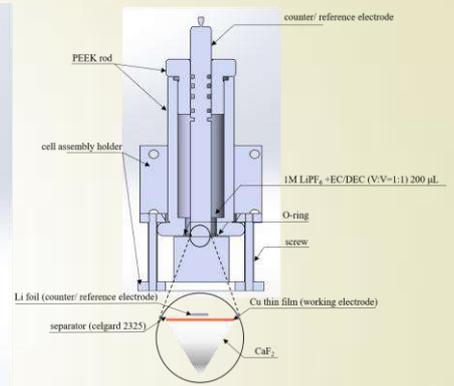
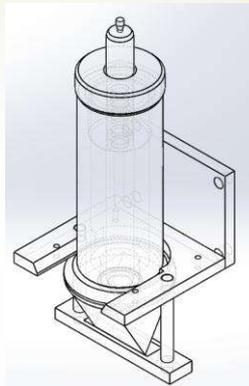
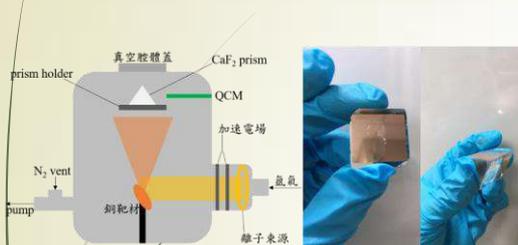


## SEI主要生成物於FTIR峰值及振動模式

含EC有機溶劑之電解質與鋰離子還原生成物在FTIR光譜中主要振動模式及峰值		
Component	Functional group	Approx. position (cm <sup>-1</sup> )
EC	VC=O	1805, 1800, 1799, 1796/ 1778, 1770, 1769
[CH <sub>2</sub> OCO <sub>2</sub> Li] <sub>2</sub>	V <sub>as</sub> C=O	1650-1640, 1688, 1663, 1656
	δCH <sub>2</sub>	1400
	V <sub>s</sub> C=O	1310-1300, 1320, 1318, 1300
	VC-O	1080, 1100-1000
	δOCO <sub>2</sub> <sup>-</sup>	830, 850-820
Li <sub>2</sub> CO <sub>3</sub>	V <sub>as</sub> C=O	1520-1450, 1500-1450, 1490-1480, 1525, 1520, 1510, 1508, 1500, 1481, 1480, 1479, 1440, 1430
	δOCO <sub>2</sub> <sup>-</sup>	880-860, 880, 875



### Method



鋰電池SEI ex-situ量測 vs. in-situ量測：

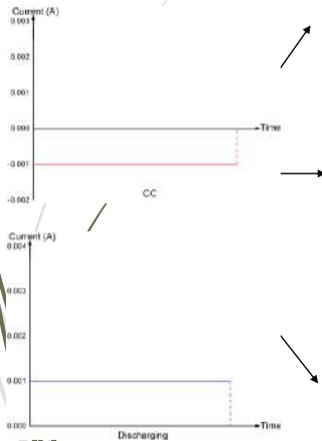
ex-situ量測係待測物到某一時間或狀態，將其與系統分離(拆解電池)進行量測，觀察範圍屬於「一個點」。雖然量測方式較簡單，但涉及電池拆解及運輸過程，SEI受大氣體影響之可能性較in-situ量測大；in-situ量測係在手套箱以特別製備的鋰電池，在其工作時同時進行量測，觀察範圍屬於「一條線」。雖然量測方式較複雜，但在電池工作時量測對待測物質狀態改變可有最即時的量測，具說服力。

綜合上述介紹，本研究將採用in-situ FTIR作為研究手法，並對SEI膜在充電法下之生成行為進行監控和觀測。



## 充電參數

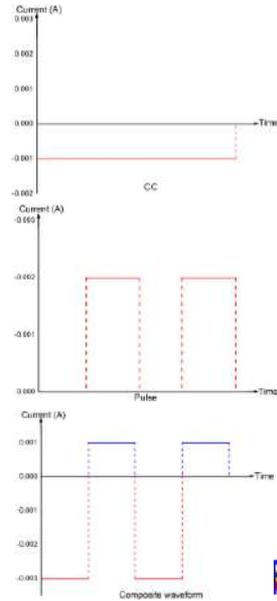
Formation before charging/discharging cycle  
 Plating (charging): -0.001A for 10 min  
 Stripping (discharging): 0.001A for 10 min,  
 voltage limit: 1V



CC :  
 Plating(charging):-0.001A for 30 min  
 Stripping(discharging):0.001A for 30 min, voltage limit: 1V

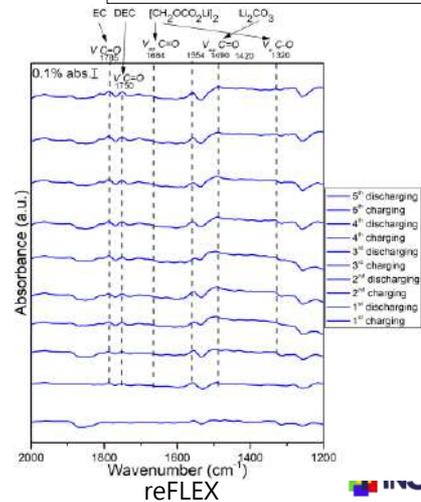
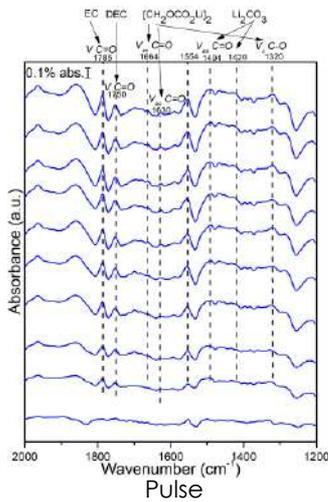
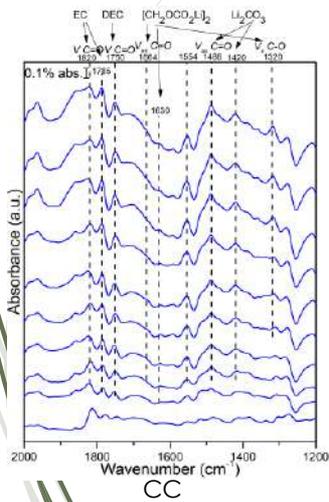
Pulse:  
 Plating(charging): -0.002A & 0A, duty: 50%,  
 frequency:1000Hz, for 30 min  
 Stripping (discharging): 0.001A for 30 min,  
 voltage limit: 1V

reFLEX:  
 Plating(charging): -0.003A & 0.001A,  
 duty: 50%, frequency:1000Hz, for 30 min  
 Stripping (discharging): 0.001A for 30 min, voltage limit: 1V



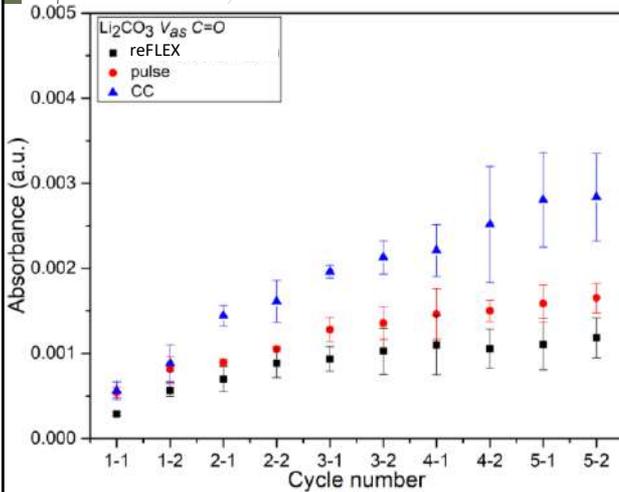
## in-situ ATR-FTIR

Li/Celgard2325/Cu  
 Background: 3.2V  
 Electrolyte : 200 $\mu$ L; 1M LiPF<sub>6</sub> in EC/DEC  
 (v : v = 1 : 1)



### in-situ ATR-FTIR

先有20分鐘的CC充放電，銅膜上已經鍍覆了一層鋰金屬，和生長SEI膜，三種充電法在 $\text{Li}_2\text{CO}_3$   $\text{V}_{as}$   $\text{C}=\text{O}$ 伸縮振動的強度隨充放電圈數走勢較穩定且規律。

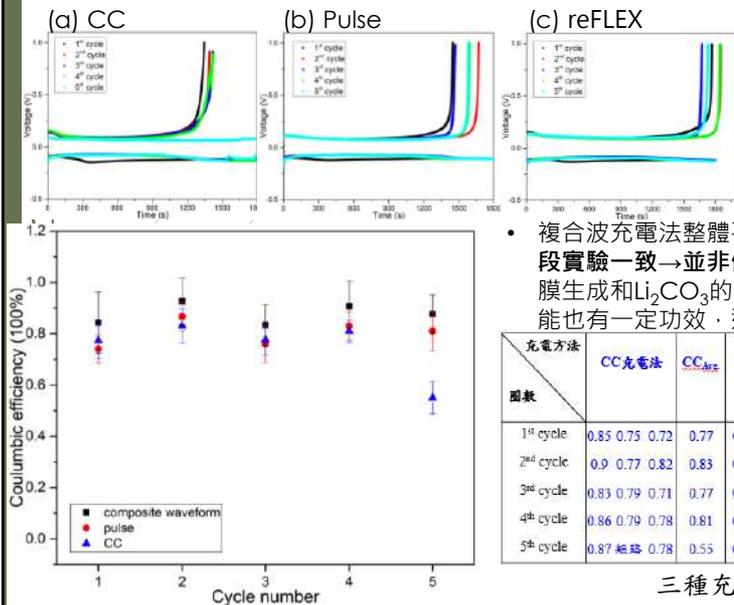


充電方法	CC充電法	CC <sub>30%</sub>	CC <sub>50%</sub>	脈衝充電法	脈衝 <sub>10%</sub>	脈衝 <sub>20%</sub>	reFLEX		
1-1	0.00044	0.00093	0.00063	0.00056	0.000107	0.00059	0.00059	0.00039	0.00029
1-2	0.00038	0.00103	0.00064	0.00089	0.000217	0.00094	0.00069	0.00077	0.00083
2-1	0.00143	0.00158	0.00135	0.00144	0.000121	0.00085	0.00091	0.00032	0.00089
2-2	0.00142	0.00189	0.00152	0.00161	0.000248	0.00105	0.00102	0.00018	0.00105
3-1	0.00202	0.00199	0.00188	0.00186	0.000074	0.00144	0.00116	0.00024	0.00128
3-2	0.00197	0.00259	0.00207	0.00213	0.000197	0.00154	0.00116	0.00037	0.00156
4-1	0.00188	0.00249	0.00226	0.00221	0.000308	0.00178	0.00119	0.00042	0.00148
4-2	0.00205	0.00330	0.00228	0.00232	0.000683	0.00209	0.00136	0.00054	0.00219
5-1	0.00263	0.00343	0.00296	0.00281	0.000956	0.00181	0.00137	0.00059	0.00169
5-2	0.00275	0.00339	0.00297	0.00284	0.000915	0.00185	0.00132	0.00059	0.00165

三種充電法的 $\text{Li}_2\text{CO}_3$   $\text{V}_{as}$   $\text{C}=\text{O}$ 伸縮振動吸收強度隨圈數比較



### 複合波充電法in-situ ATR-FTIR



- CC充電法有出現短路現象→除了使SEI膜增厚，產生過多的dead Li和鋰枝晶的形成刺穿隔離膜而使得電池短路。
- 脈衝充電法整體平均值位於二者中間→休息區間有效，但不比複合波充電法的放電區間。

- 複合波充電法整體平均值最高，也有出現超過100%的圈數，與第一階段實驗一致→並非偶然，放電區間逆還原反應效果，除了可以抑制SEI膜生成和 $\text{Li}_2\text{CO}_3$ 的成長，對於鋰鍍覆的完整性和抑制dead Li的生成可能也有一定功效，造成類似電池活化的成果。

充電方法	CC充電法	CC <sub>30%</sub>	CC <sub>50%</sub>	脈衝充電法	脈衝 <sub>10%</sub>	脈衝 <sub>20%</sub>	reFLEX		
1 <sup>st</sup> cycle	0.85	0.75	0.72	0.77	0.068	0.73	0.80	0.69	0.74
2 <sup>nd</sup> cycle	0.9	0.77	0.82	0.83	0.065	0.87	0.92	0.81	0.86
3 <sup>rd</sup> cycle	0.83	0.79	0.71	0.77	0.061	0.78	0.82	0.68	0.76
4 <sup>th</sup> cycle	0.86	0.79	0.78	0.81	0.043	0.78	0.89	0.82	0.83
5 <sup>th</sup> cycle	0.87	0.78	0.78	0.55	0.063	0.82	0.88	0.73	0.81

三種充電法的充放電庫倫效率比較



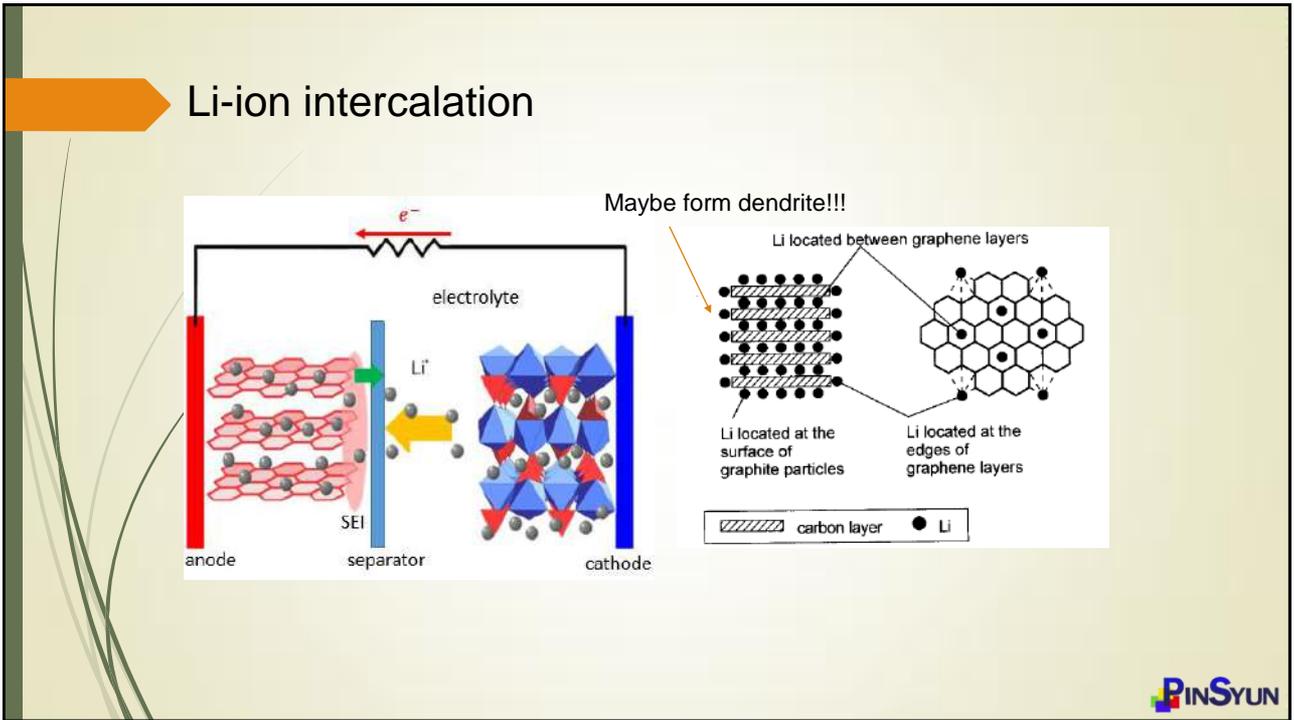
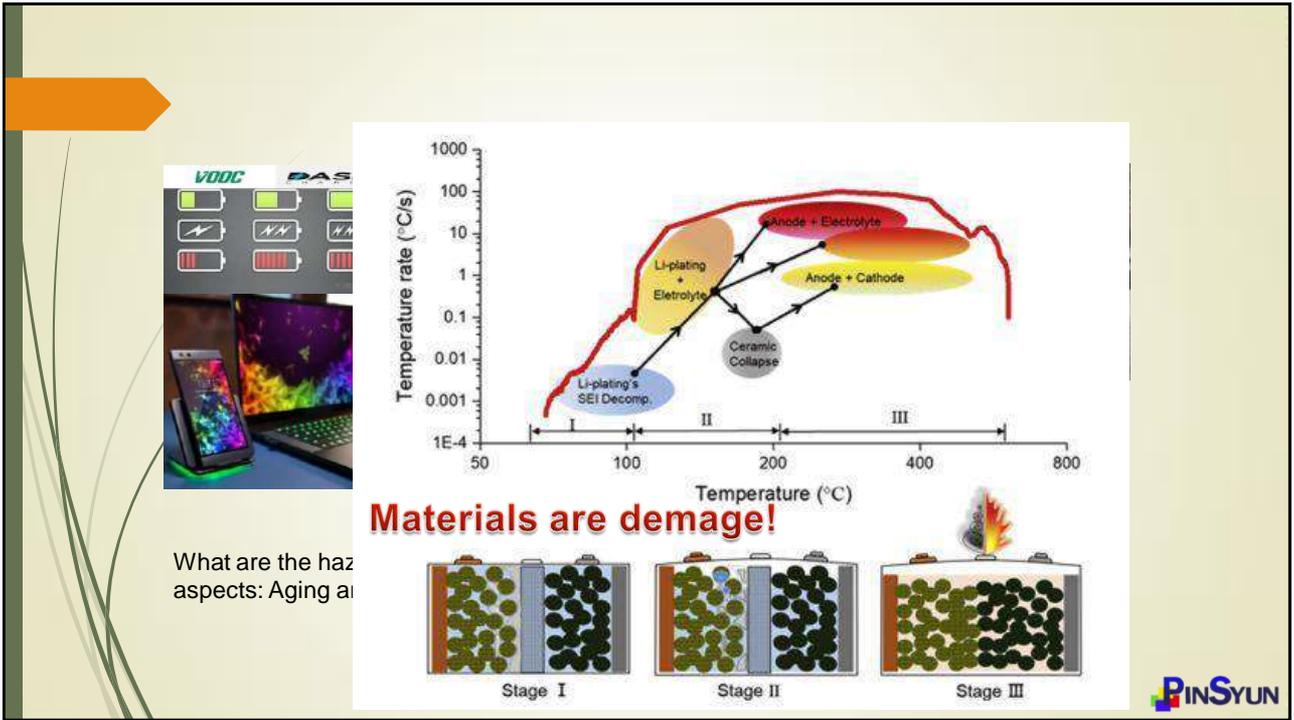
## 結論

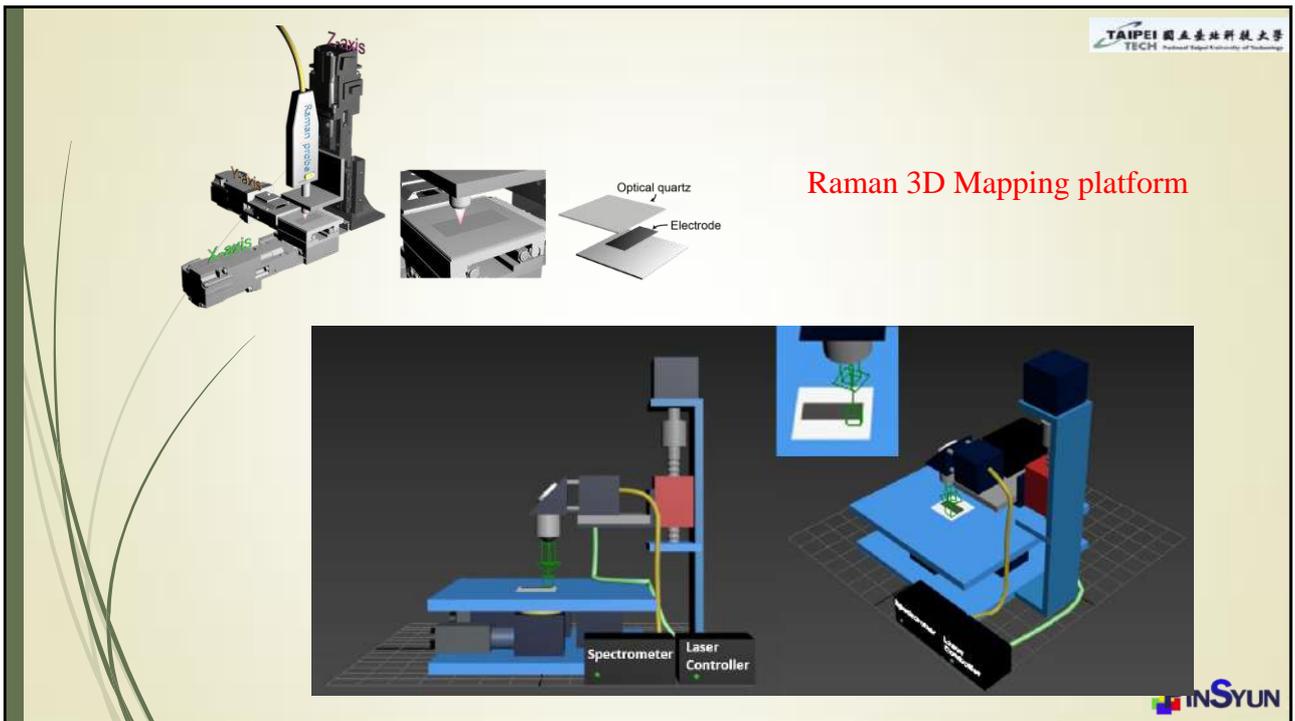
- reFLEX充電法作用FTIR強度為三者中最低，代表其 $\text{Li}_2\text{CO}_3$ 的生成最少，越能抑制 $\text{Li}_2\text{CO}_3$ 的生成。
- 脈衝充電法位於兩者間，代表其休息區間固然有一定功效，但不比reFLEX充電法的放電區間逆還原反應之功效，更能有效抑制 $\text{Li}_2\text{CO}_3$ 的生成。
- CC充電法有出現短路現象，除了較無法抑制 $\text{Li}_2\text{CO}_3$ 的生成，可能也造成了dead Li甚至是鋰枝晶的生成，而穿刺隔離膜造成短路。
- reFLEX充電法整體平均最高，甚至出現超過100%的充放電庫倫效率的圈數，與第一階段實驗一致，是唯一充放電庫倫效率皆有超過100%的充電方法，不是偶然現象。  
→放電區間相較休息區間，除了有逆還原反應可抑制 $\text{Li}_2\text{CO}_3$ 的生成，也可能具備使鋰鍍覆更加完整且平均，減少dead Li的生成，帶來類似電池活化的結果，使得經複合波充電法作用的電池，既可抑制 $\text{Li}_2\text{CO}_3$ 的生成，也能提供穩定的充放電庫倫效率，是對鋰電池的充電為三種充電法中最有助益的方法。



## The challenge of fast-charging







## Fast-charging strategy

4.5V  
3.8V  
3.7V  
1ms

**CC-reFLEX**  
The fast-charging strategy in this study

4.1V  
3.8V

**CC-CV (voltage 4.1V)**  
Control experiment

According to the specifications of the battery, we set the fast-charging strategy based on reFLEX charging method.

**3C charging**  
1C discharging

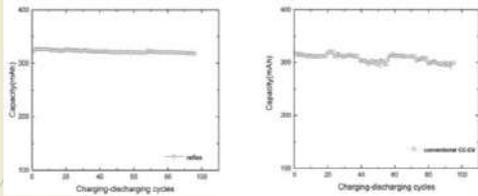
Separator  
Positive Electrode  
Negative electrode

Model: htc-50PL6100  
Voltage: 3.8 VDC

**PINSYUN**

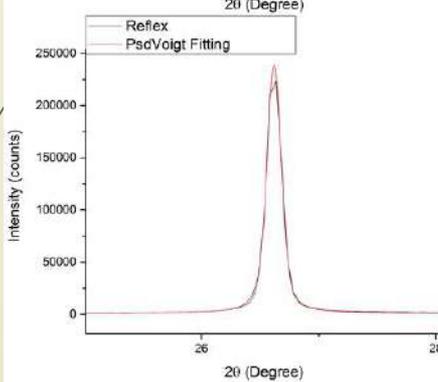
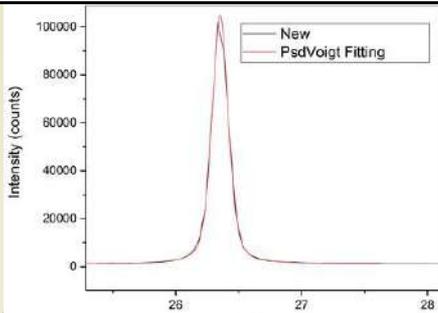
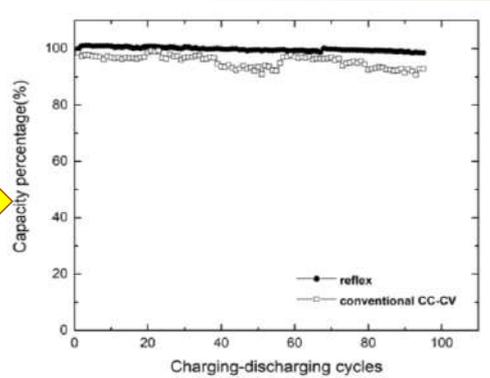
## Results and Discussion

### Capacity



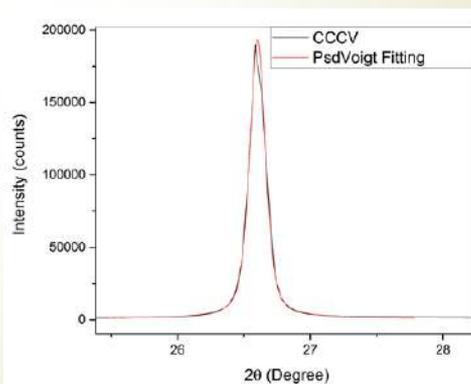
Capacity after 100 cycles charging and discharging

CC-CV method and Reflex fast-charging method batteries' capacity compared.



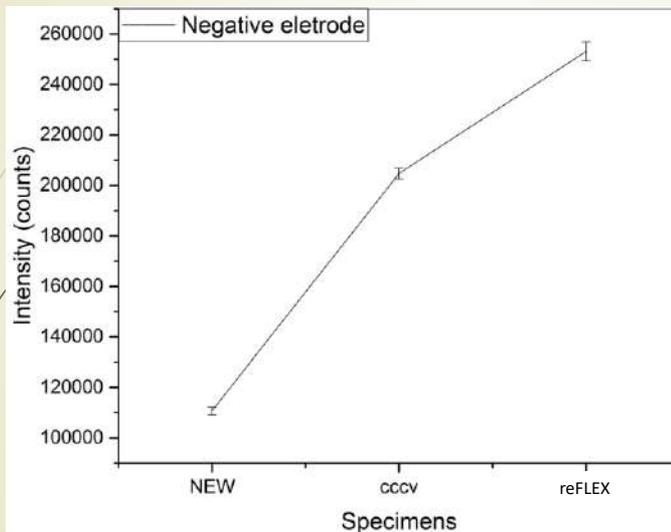
Pseudo-Voigt function:

$$y = y_0 + A \left[ m_u \frac{2}{\pi} \frac{w}{4(x-x_c)^2 + w^2} + (1 - m_u) \frac{\sqrt{4 \ln 2}}{\sqrt{\pi} w} e^{-\frac{4 \ln 2}{w^2} (x-x_c)^2} \right]$$



## Results and Discussion

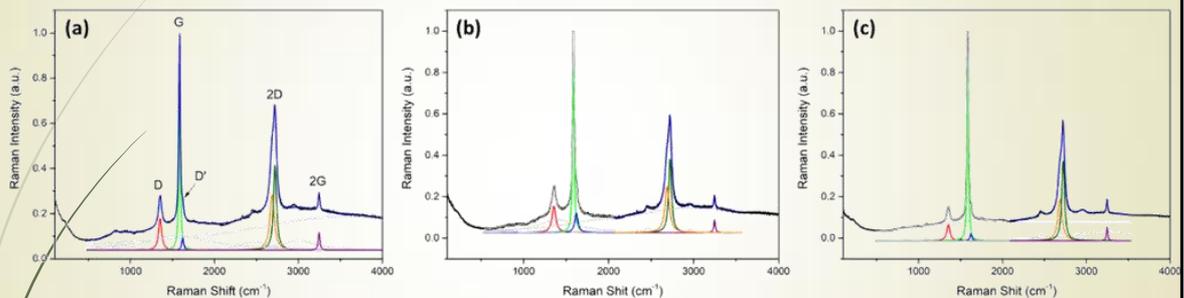
XRD



reFLEX and the CCCV are able to improve the quality of the graphitic negative electrode by comparing the intensity of the (002).

## Results and Discussion

Raman



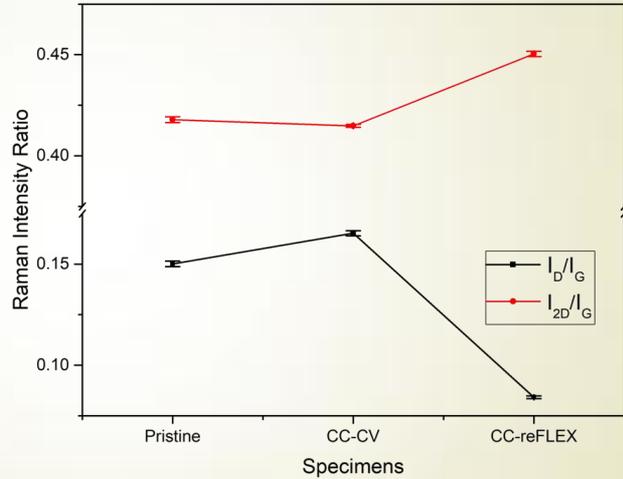
Raman spectra of negative electrodes from (a) a battery charged through CC-reFLEX charging, (b) and unused battery, and (c) a battery charged through the CC-CV method. In each picture, the upper curve is the average spectrum from 10 × 10 points; the lower curve is the spectrum after fitting.

## Results and Discussion

### Raman fitting

We can get the intensity of  $I_D/I_G$  the result is need smaller is better. So we can see the Reflex method is better than CC-CV.

And CC-CV method does cause carbon defects.  $I_{2D1}/I_G$  &  $I_{2D2}/I_G$  which results are big as better. Therefore, we can see that reFLEX fast-charging method is as good as Pristine and CC-CV.



Raman fitting results

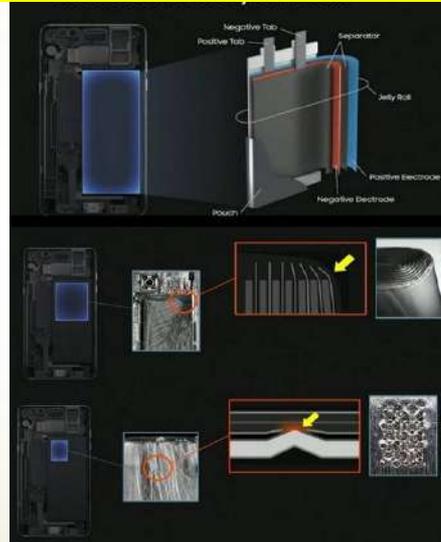
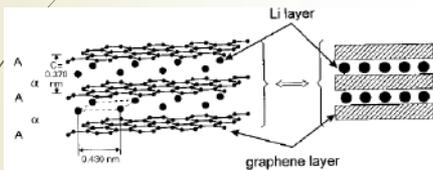


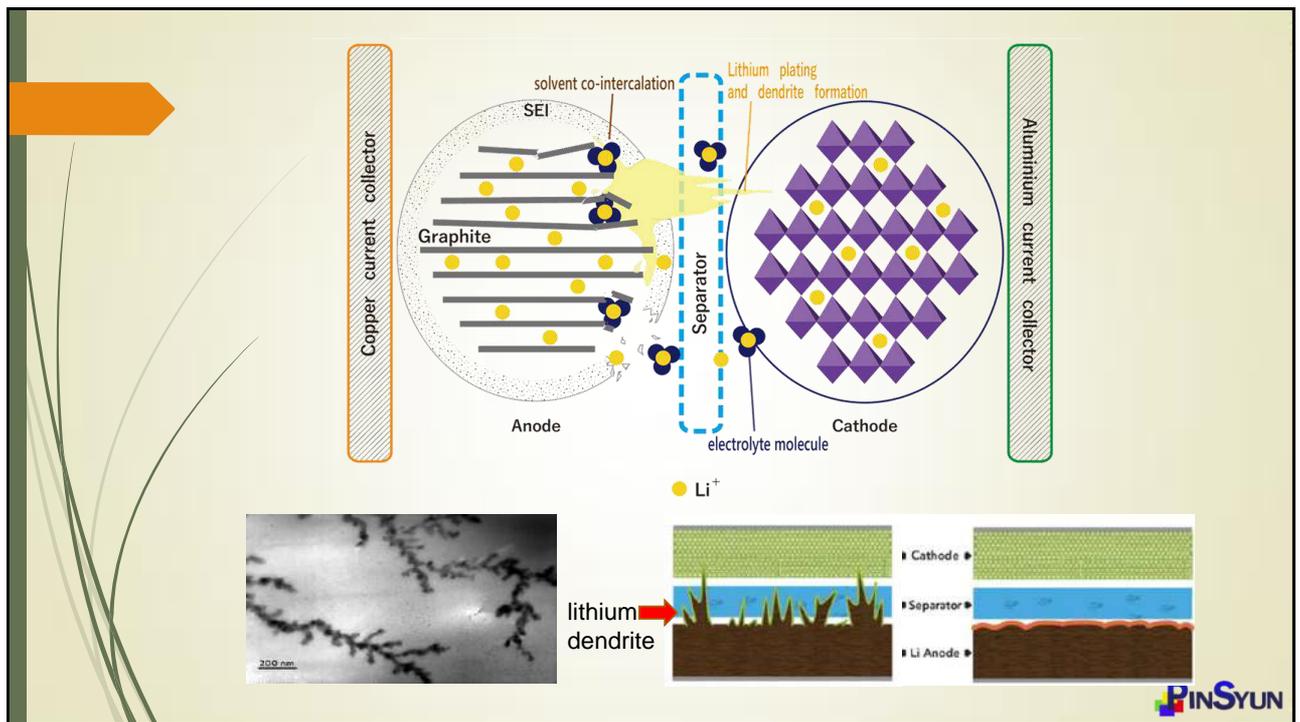
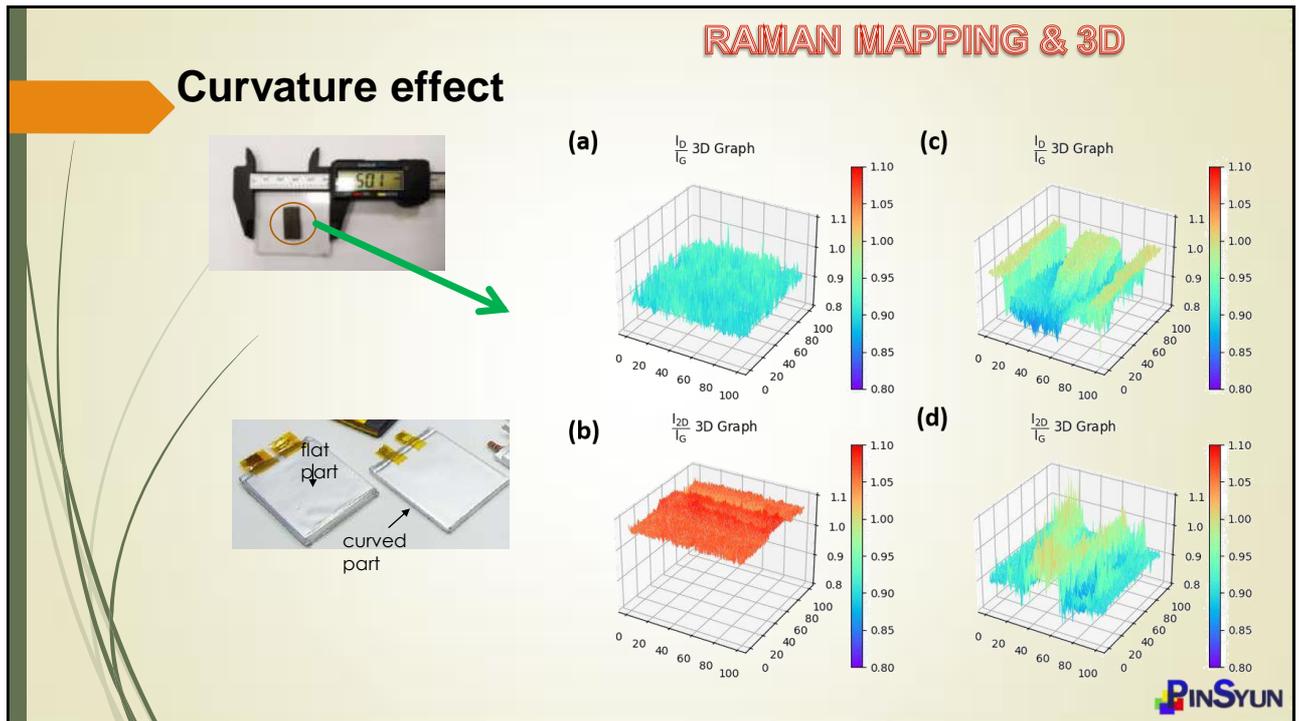
## Shape induced curvature effect

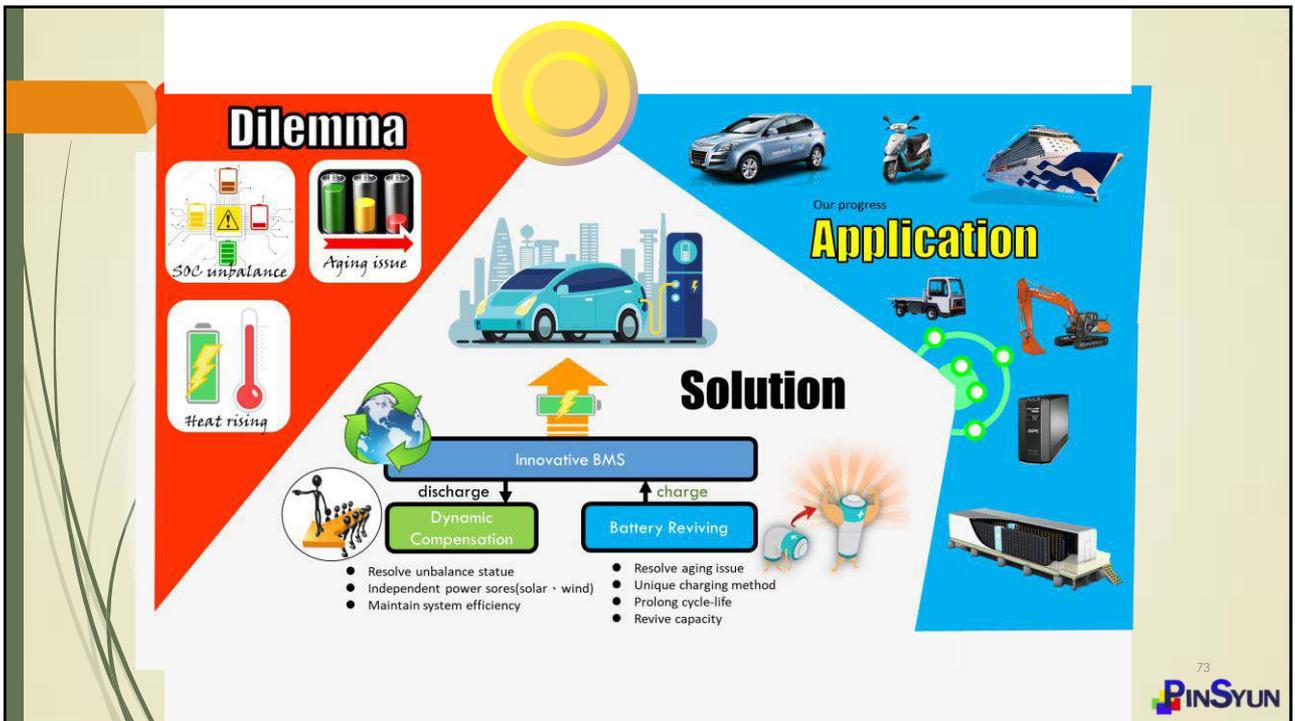
Remember the serial explosion of Samsung note7 mobile phones? **Samsung Note 7 battery structure and its fail reasons**

Battery cell Shape induced curvature effect is very important!

**BUT, WHY???**







Thanks for your attention.