中美关于二次电池及相关能源材料基础研究的合作与交流

China-US Cooperation and Exchanges in Basic Research on Secondary Batteries and Energy Maerials

吴锋

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2012.8.23（波士顿Boston）

早上6点离开酒店，到达华盛顿杜勒斯机场，赶上了机场的日出
Leave the hotel at 6 AM, and catch a sunrise in Dulles Int’l Airport(IAD)

晚上8点到达波士顿前的飞机上，看到了天空中的日落。
8 PM, in the airplane above Boston, a sunset in the sky.

关于中美动力电池合作交流的回顾
Review of the Cooperation in Power Batteries Between China and US

我们这个会议已经成功举办了5届，从北京－芝加哥－杭州，到今天的波士顿，它是一个纽带，拉近了我们之间的距离，促进了相互之间的了解，逐渐形成了一些共识，建立了友谊，推动了合作。首先让我们对上一次杭州会议及相关交流做一个简短的回顾。

This meeting has been hold successfully for 5 times, from Beijing to Chicago, and then Hangzhou, till Boston today, it links us together and offer a platform to know well with each other, to gradually form common views, to build up good friendships and promote impressive cooperation.

First of all, Let us review our last meeting in Hangzhou and some related collaborations.

5th China-US Electric Vehicles and Battery Technology Workshop

West Lake National Hotel, Hangzhou, China, Apr. 16-17,2012

春天西子湖畔如画般的美景，也为我们的会议增添了色彩！

The picturesque view by the West Lake in this spring made our workshop even better.

5th China-US Electric Vehicles and Battery Technology Workshop, Hangzhou, China

会议现场

5th China-US Electric Vehicles and Battery Technology Workshop, Hangzhou, China

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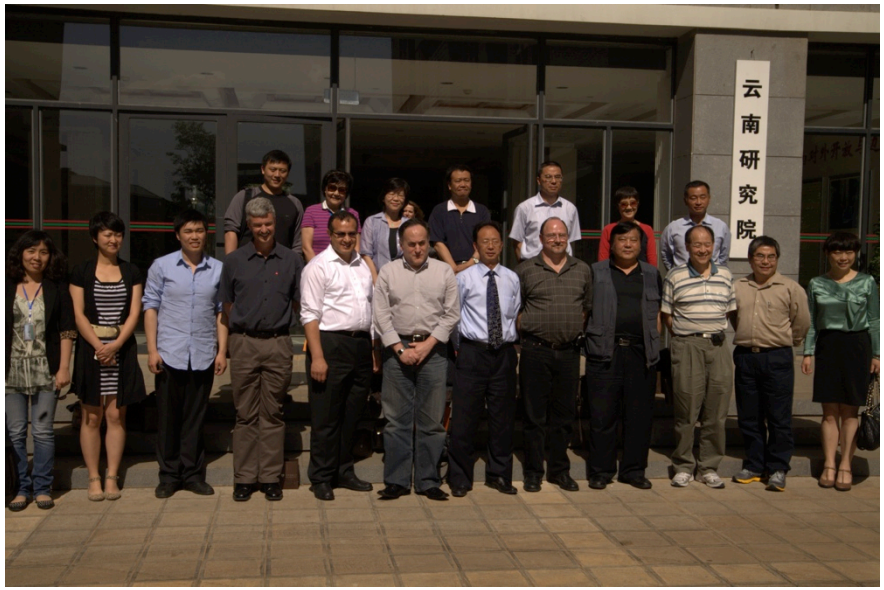
参观云南石林光伏发电站 Visiting Yunnan Shilin PV Power Station

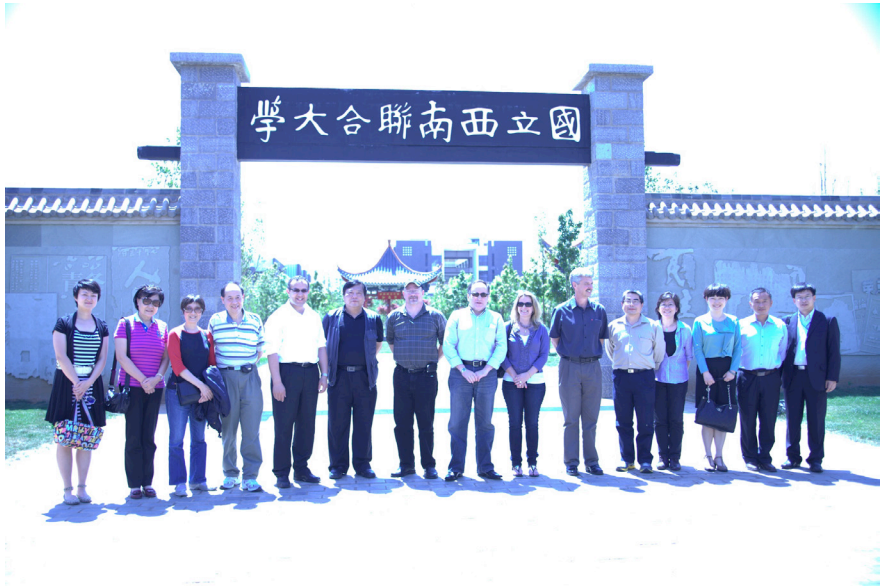
云南的光伏发电也是一道迷人的风景线！

PV Power Station located in YunNai province is a beautiful sightseeing.

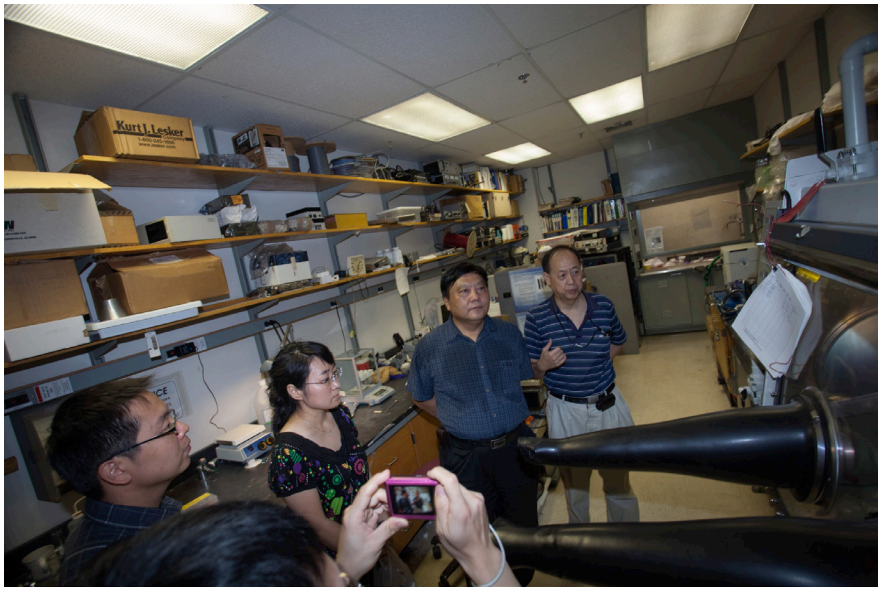
参观云南石林光伏发电站
Visiting Yunnan Shilin PV Power Station

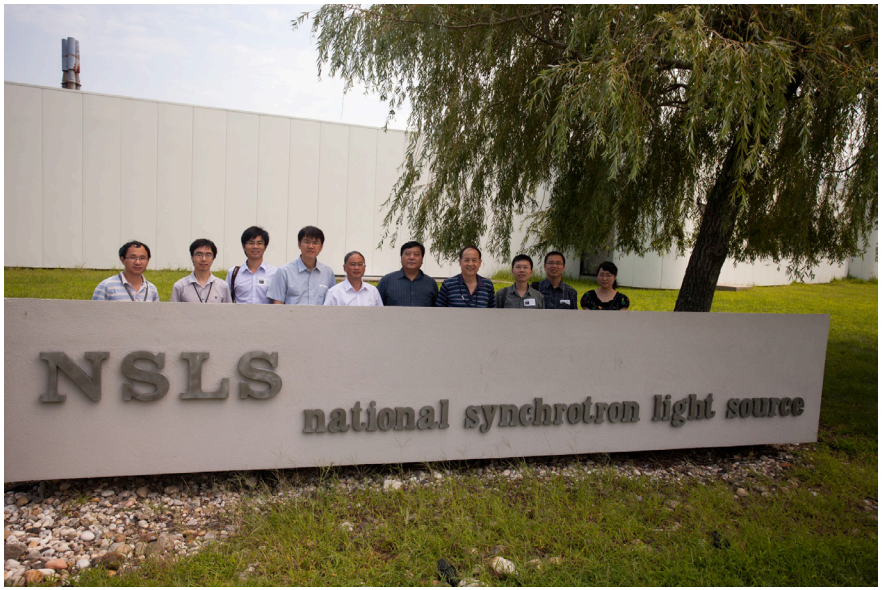
参观云南师范大学（其前身为著名的西南联大）
Visiting Yunnan Normal University（Former National South-west Joint University）





BIT research group visited BNL on Aug 17th2012





中国政协教科文委员会主任、原科技部部长徐冠华院士十分关注电动汽车和动力电池技术的发展。他去年曾专程到北京理工大学电池实验室参观考察，对相关研究工作和中美动力电池技术的合作交流给予了高度评价。

Guanhua Xu, Member of China Academy of Science, Director of Technology, Education, and Culture Division in CPPCC, former minister of MOST, is concerning about the technology development of electric vehicles and power batteries. He visited the battery laboratory in BIT and gave a positive praise on the cooperation in power battery between US and China.

“10 cities -1000 Vehicles ”Large Scale Demo Program

To promote a three-year long “10 cities---1000Vehicles”Large Scale Demonstration Program in selected cities.

New energy vehicle are firstly applied in public transportation system.

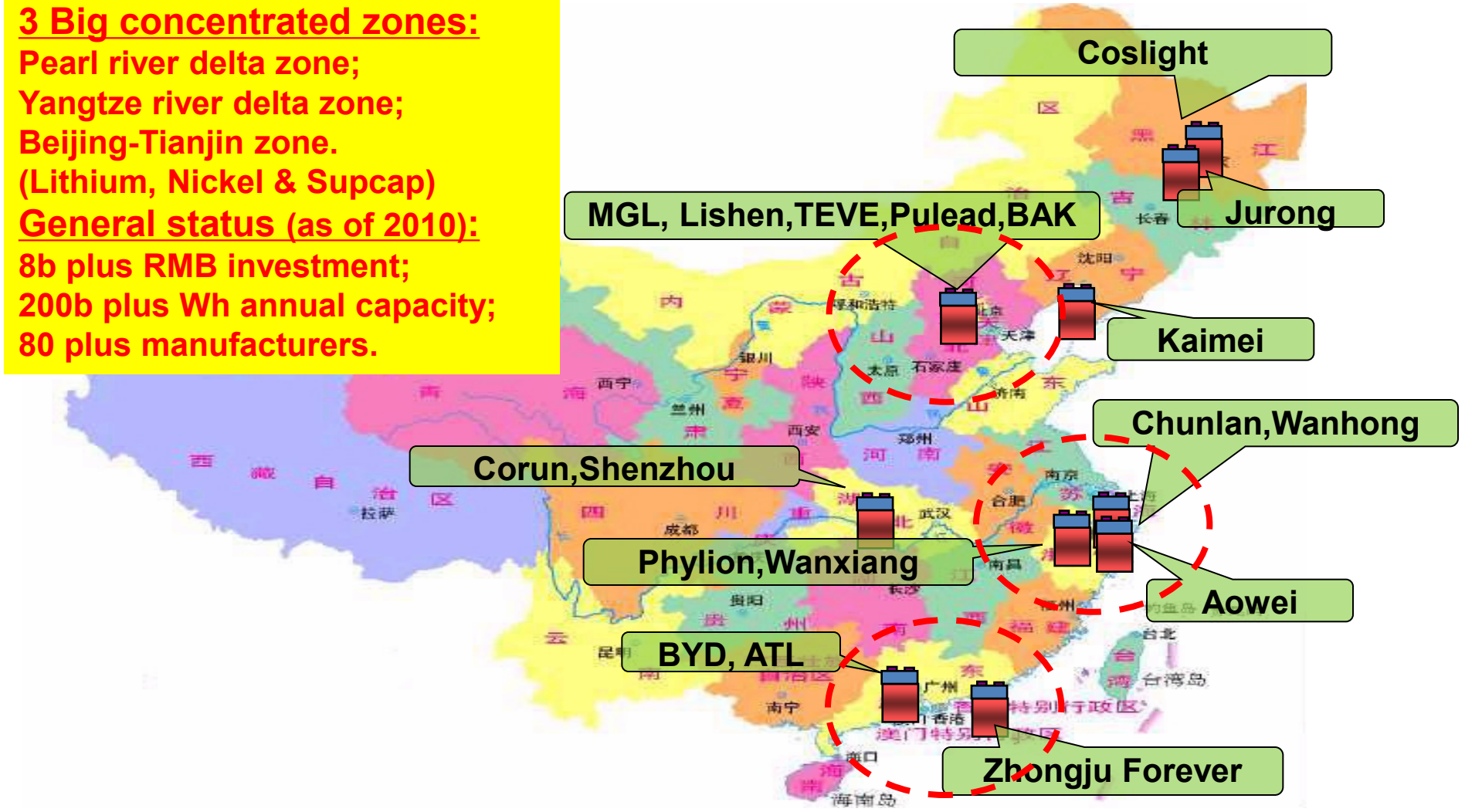
Subsidy from government to operation department is available to offset the price difference between new energy vehicle and traditional vehicle.

100k plus electric vehicles will be demonstrated during 3 years.

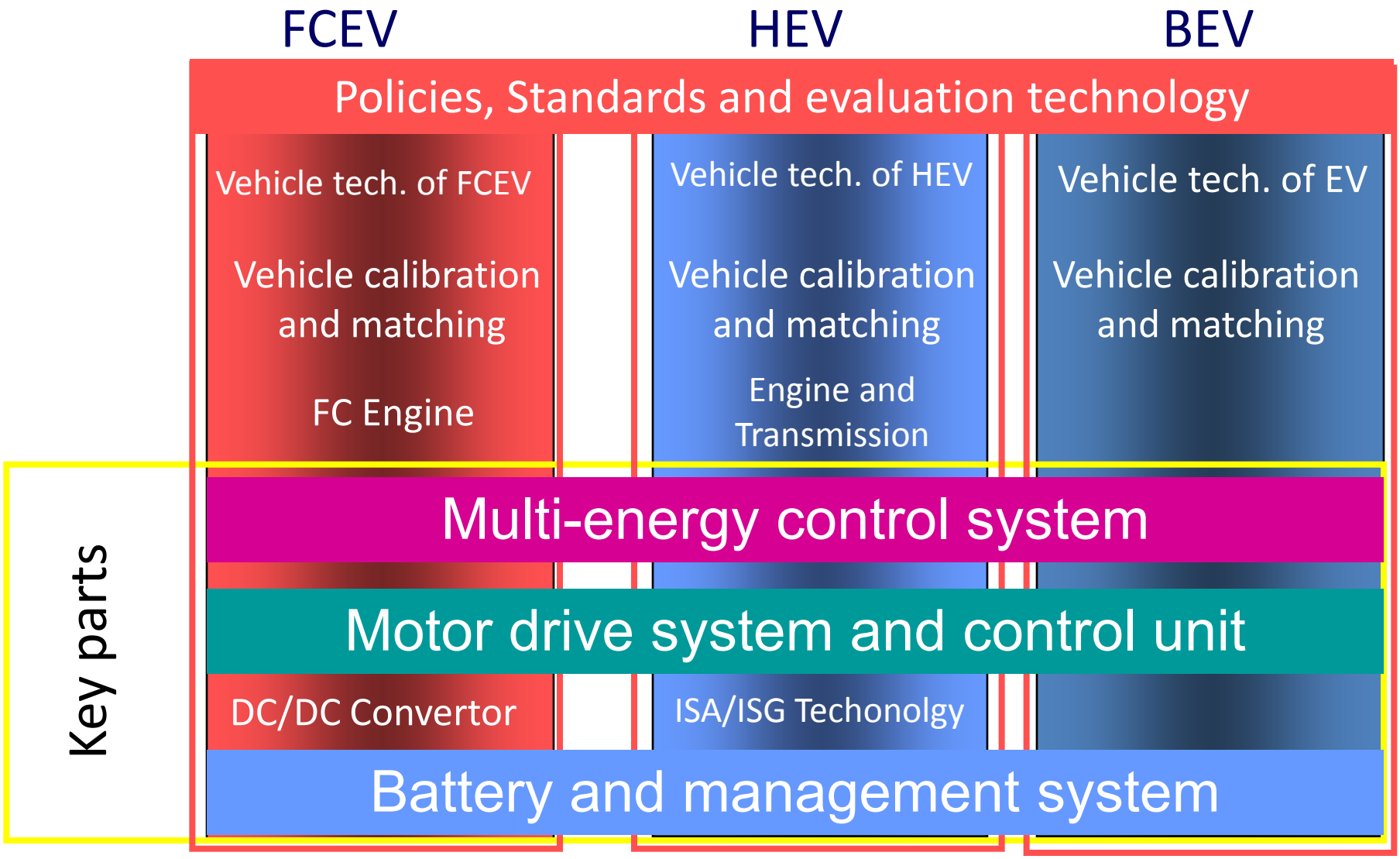
Layout of power battery manufacturers for electric vehicles

3 Big concentrated zones:
Pearl river delta zone;
Yangtze river delta zone;
Beijing-Tianjin zone.
(Lithium, Nickel & Supcap)

General status (as of 2010):
8b plus RMB investment;
200b plus Wh annual capacity;
80 plus manufacturers.



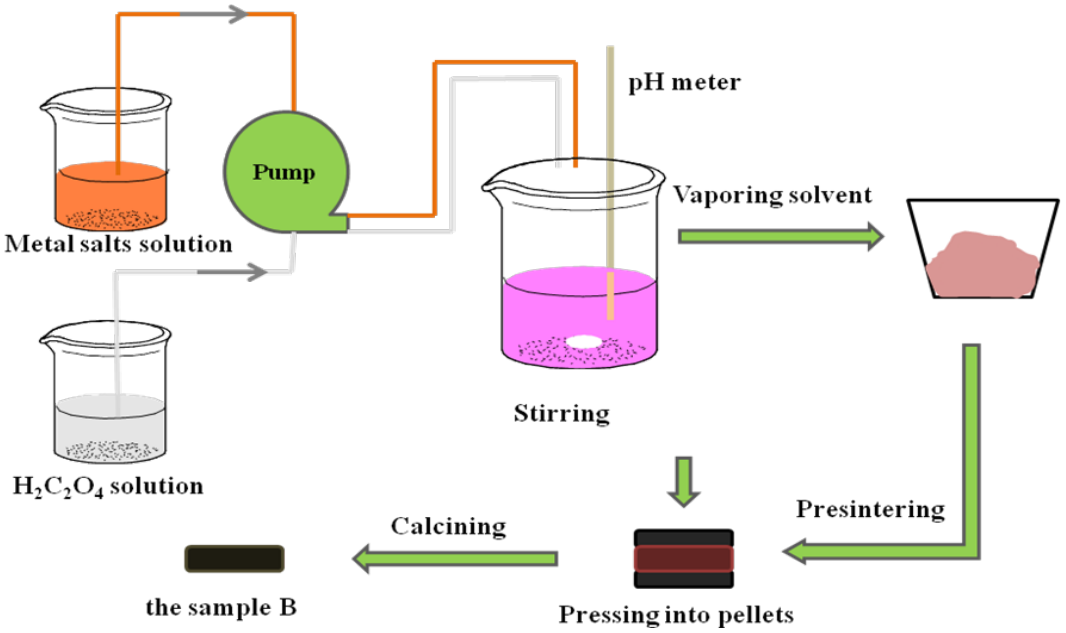
National new energy vehicle key project layout: Three verticals and Three parallels



高比能锂离子电池与相关正极材料

High power Li-ion batteries and related cathode materials

草酸直接共沉淀法合成富锂材料
$Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$
Synthesis of lithium rich cathode materials by a direct co-precipitation method



Synthetic process

合成工艺

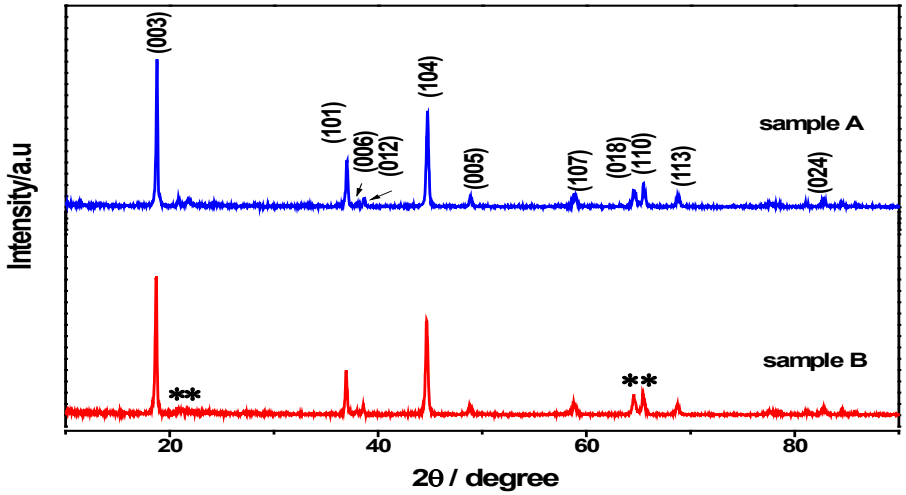
A direct co-precipitation method with oxalic acid to synthesize (草酸直接共沉淀法合成) $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$

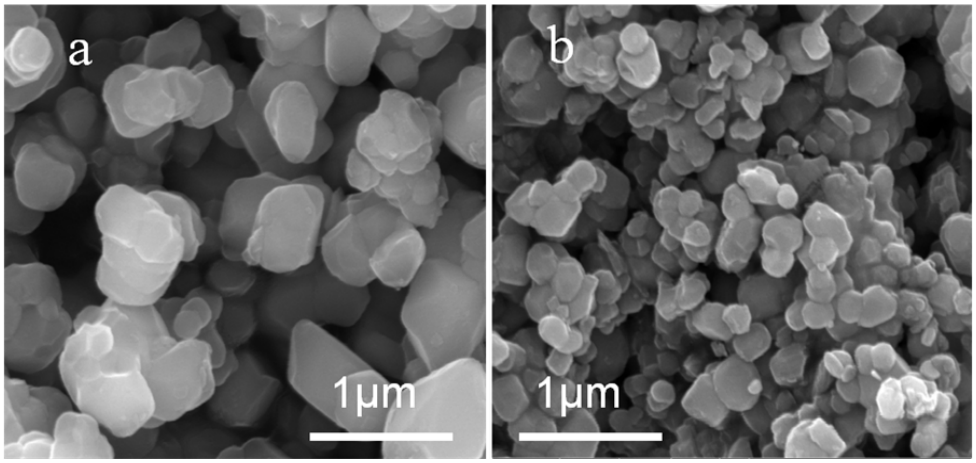
•Solution（溶剂）：Ethanol

• Precipitator（沉淀剂）：$H_2C_2O_4$

Precipitate Mn^{2+}, Ni^{2+}, Co^{2+} as well as Li^{+} in ethanol solution at the same time. (Mn^{2+}, Ni^{2+}, Co^{2+}和Li^{+}在乙醇溶液中同时沉淀下来)

结构与形貌分析
Structure and morphology analysis

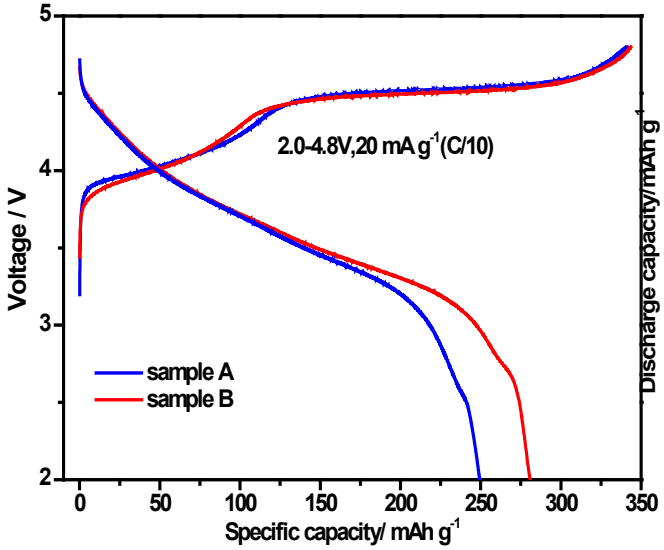


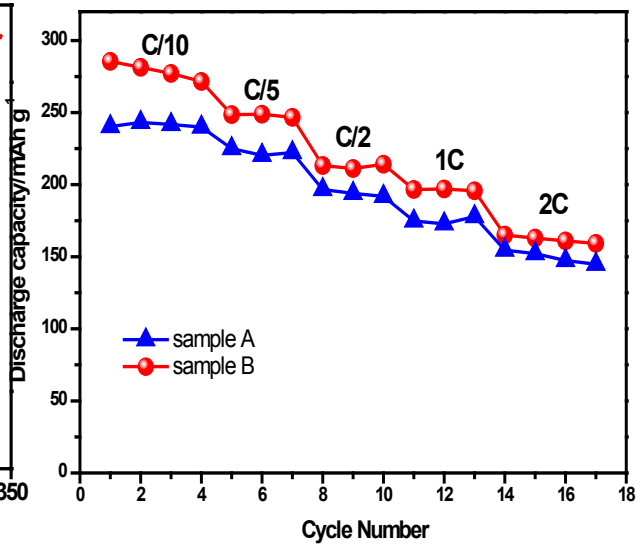


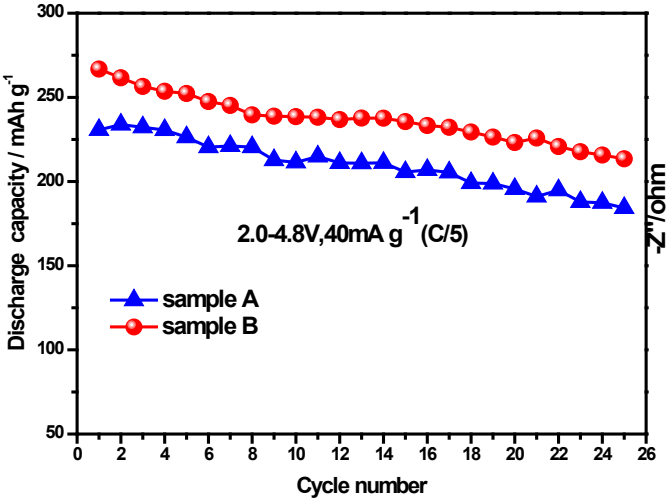
- Hexagonal α-$NaFeO_2$ structure (*R*-3*m*)，super-lattice corresponding to Li_2MnO_3
- 两种材料都具有六方相α-$NaFeO_2$层状结构和20-25度间超晶格峰，与之前文献报道相符合！
- Both of the materials is quite homogeneous with quasi-sphere shapes, but particles of the sample B have smaller sizes.
- 两种材料颗粒相貌都呈类球形且分布均匀，但样品B具有更小的粒径。

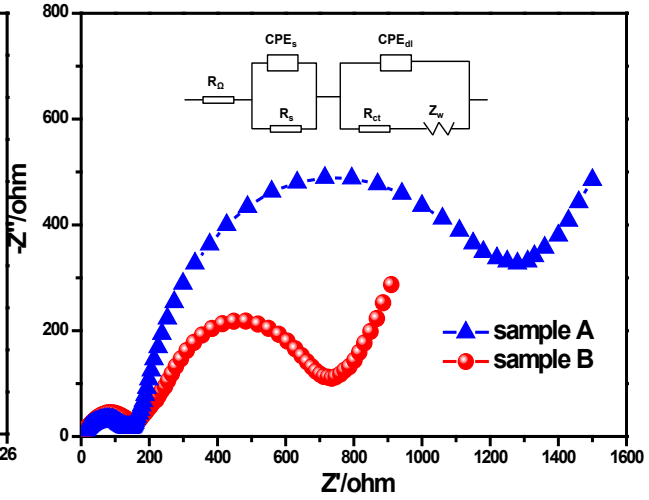
sample A :Conventional Co-precipitation with $(NH_4)_2C_2O_4$ as the precipitator in the aqueous
sample B :Direct Co-precipitation with oxalic acid （草酸直接共沉淀法）

样品电化学性能
Electrochemical properties of two samples









Sample B shows high discharge capacity up to its theoretical value;

It exhibits smaller irreversible capacity loss and better rate performance than sample A.

材料B（草酸直接共沉淀法）首次放电容量280.8mAh/g（接近理论容量293mAh），与样品A相比，其不可逆容量损失更小，倍率性能更佳。

This simple method is possible for industrial production and our work may give a new insight for designing Li-rich cathode materials for the next generation Li-ion batteries.

这种新的合成方法可能用于材料的商业化生产，也为下一代高性能的锂离子电池富锂材料正极材料的设计提供了一些思路。（两种材料均未进行任何改性处理，所以循环稳定性和倍率性能有待进一步改善）

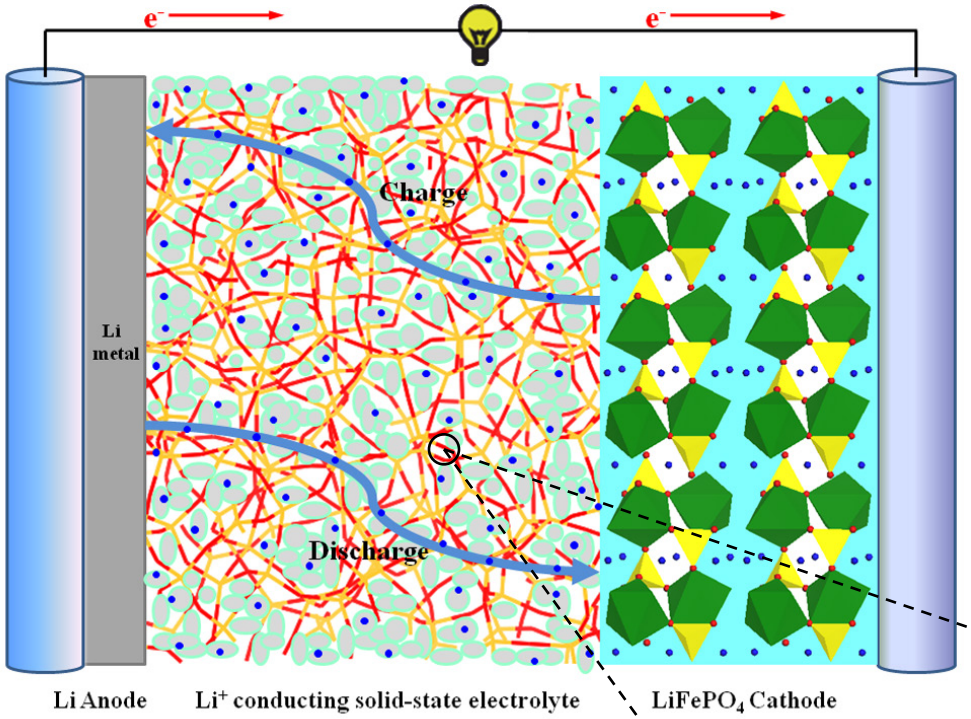
固态化锂离子电池构造

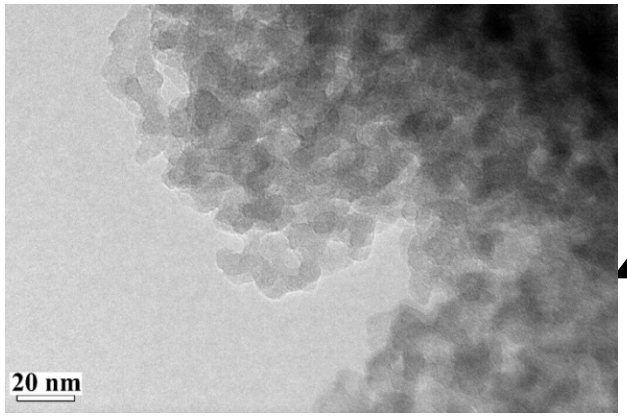
Solid-state battery configuration

$LiFePO_4$/composite electrolyte/Li

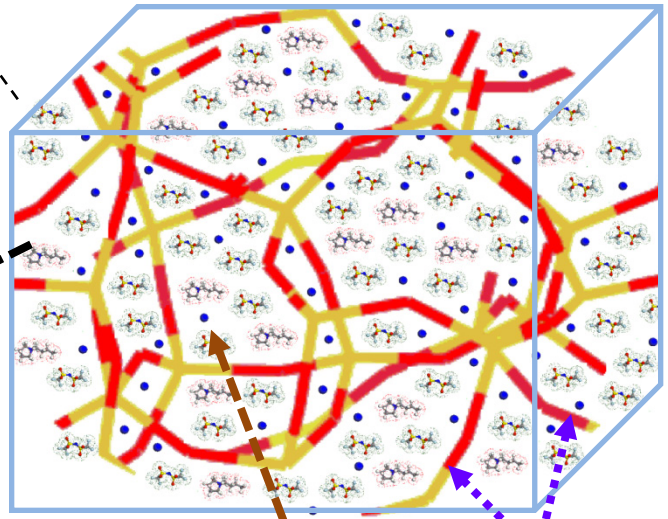
原位组装制备介孔SiO_2复合离子液体电解质,具有较高的离子电导率(10^{-3} S cm^{-1}).

Composite electrolyte: mesoporous silica matrices in-situ immobilizing lithium ion conducting ILs, It can be pictured as two interpenetrating continuous phase (silica matrix and ILs) intermingled at molecular scale, ionic conductivity of 10^{-3} S cm^{-1}.





Mesoporous matrix (TEM)



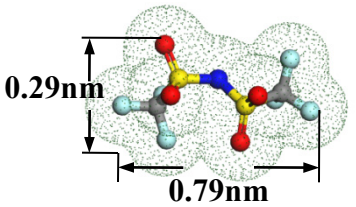
Average pore size D=7nm

SiO_2 walls

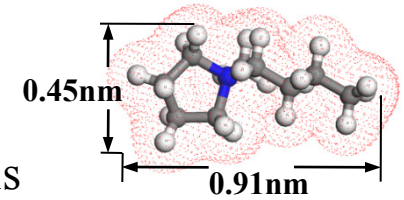
Li Cation

0.15nm

TFSI Anion

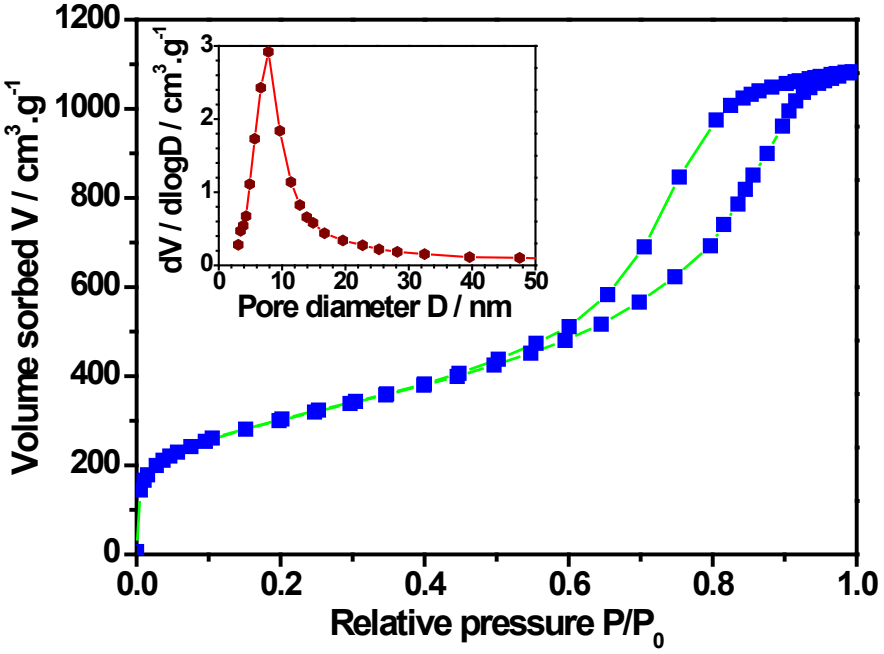


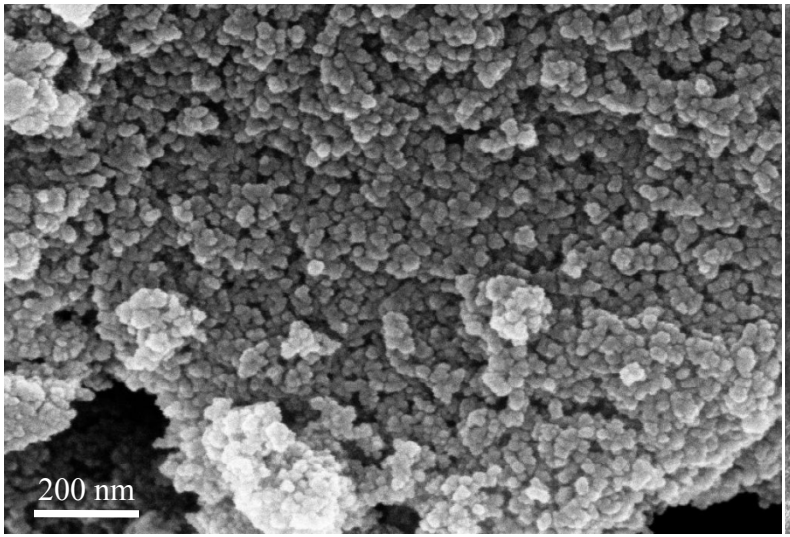
BMP Cation



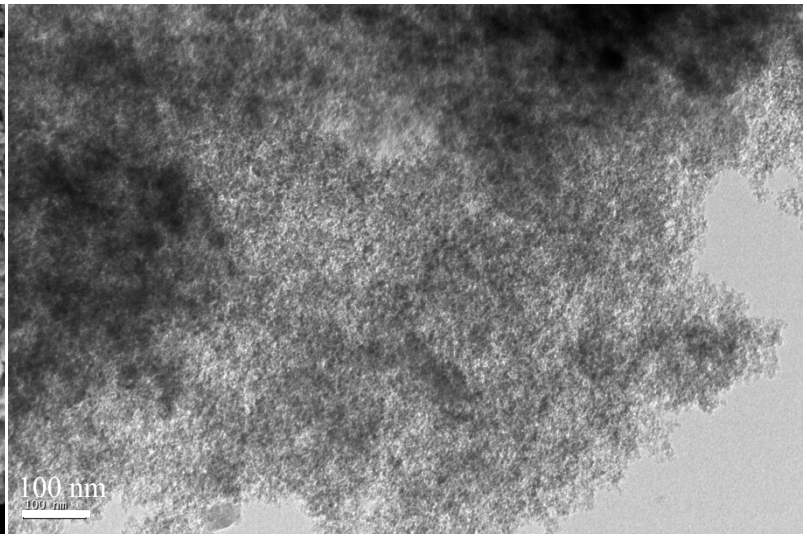
由吸附了离子液体的介孔硅基网络形成的复合电解质, 其硅基网络具有丰富的孔道结构和比表面积,表现出较高的吸附容量.

The silica matrix has a high open porosity confirmed by N_2 sorption measurement. The specific surface area and pore volume of the porous matrix were 1078 m^2/g and 1.68 cm^3/g, respectively.



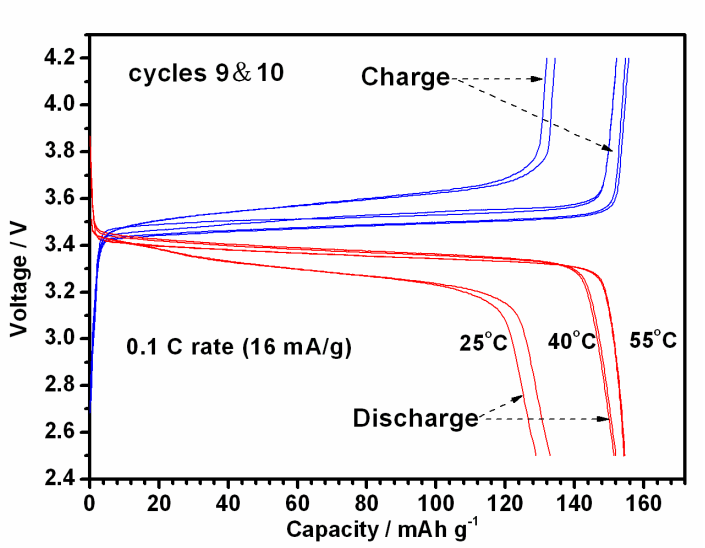


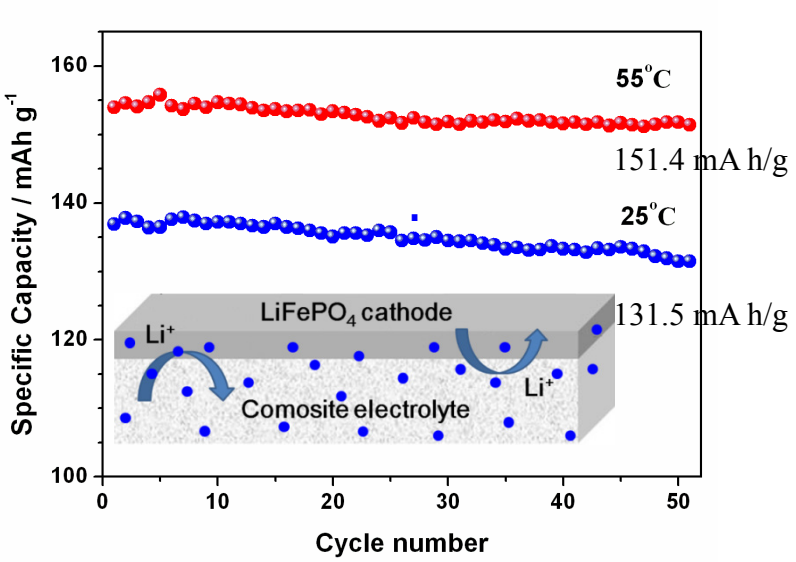
SEM image



TEM image

电池具有良好的高温性能
The Battery reveals a good high temperature performance





该电池表现出良好的高温性能, 表明电解质与电极具有良好的兼容性，电解质材料具有良好的结构稳定性能，电池倍率性能优于全固态锂电池。

The cell exhibited a high reversible capacity and excellent cycling performance at 55 ◦C, These was attributed to the excellent electrode-electrolyte compatibility and its structural integrity at high temperature .These cells exhibited a better rate performance than all-solid-state lithium batteries.

Project: Battery Implementation-Vehicle Battery Recycling in China and U.S.

中美合作研究课题—电动汽车用动力电池的资源化回收应用

北理工—阿岗（BIT—Argonne）

Technical Approach 合作内容

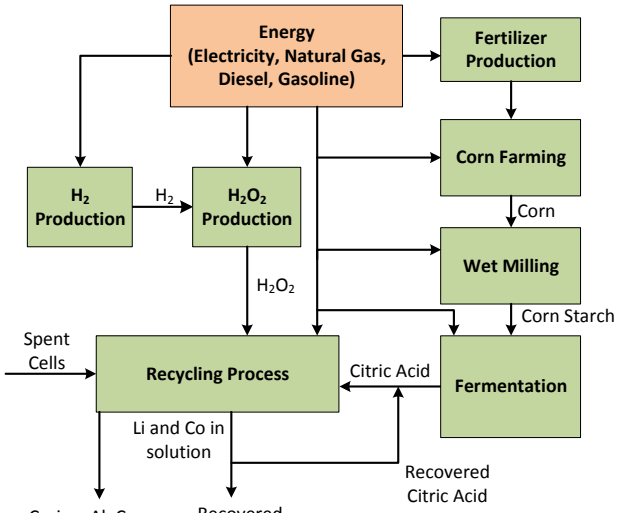
- **Identify and characterize promising recycling technologies in both countries**
- **Compare best practice to identify potential improvements**
- **Evaluate the performance and economical need for batteries in applications of EV.**
- **The GREET Vehicle-Cycle Model was used to examine life-cycle implications of BIT-patented battery recycling technologies.**

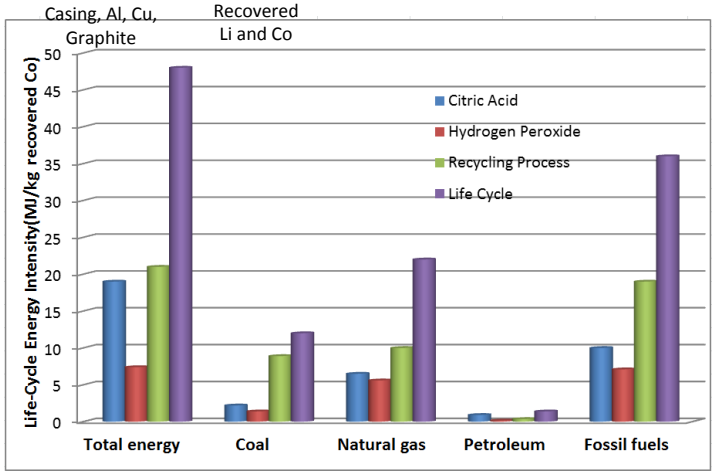
- **研究分析双方具有潜力的电池回收技术；**
- **研究电极材料的低成本回收再生应用技术；**
- **评估电动汽车对动力电池的性能与经济性要求；**
- **基于北理工的电池回收技术授权专利与阿岗开发的GREET模型，研究电池的回收与生命周期评价。**

L.Li, J.B.Dunn , X.X.Zhang, L.Gaines , F. Wu , M. Wang . Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and LCA. Submitted to EES.

中美双方的合作工作成果已投稿EES。

Initial Results 初步结果





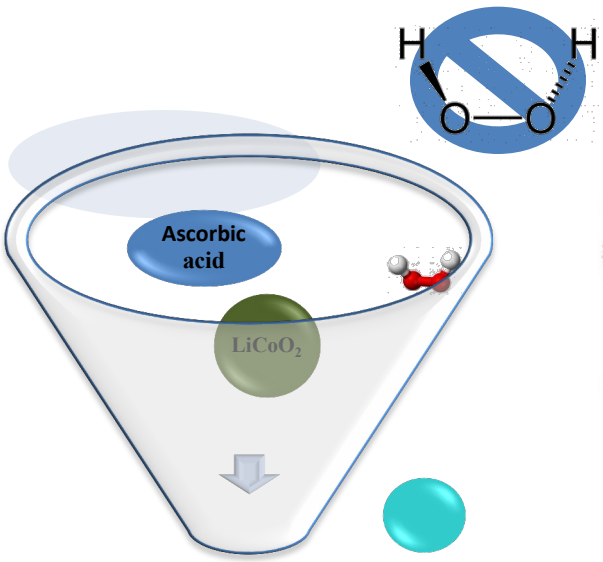
抗坏血酸对废旧电池中金属离子的浸提研究

Ascorbic-acid-assisted recovery of cobalt and lithium from spent LIBs

又名维生素C
Vitamin C

- 抗坏血酸是一种天然存在的具有抗氧化性质的有机化合物，具有酸性及还原性。采用抗坏血酸作为浸出剂和还原剂，对废旧锂离子电池进行回收处理，具有较高的金属离子浸出率。

Organic ascorbic acid is a naturally occurring organic compound that behaves as a vinylogous carboxylic acid as well as a mild reducing agent. we have designed and tested an ultrasonic-assisted hydrometallurgical technique using ascorbic acid as leaching reagent and reducing agent for recovery of cobalt and lithium from spent LIBs.



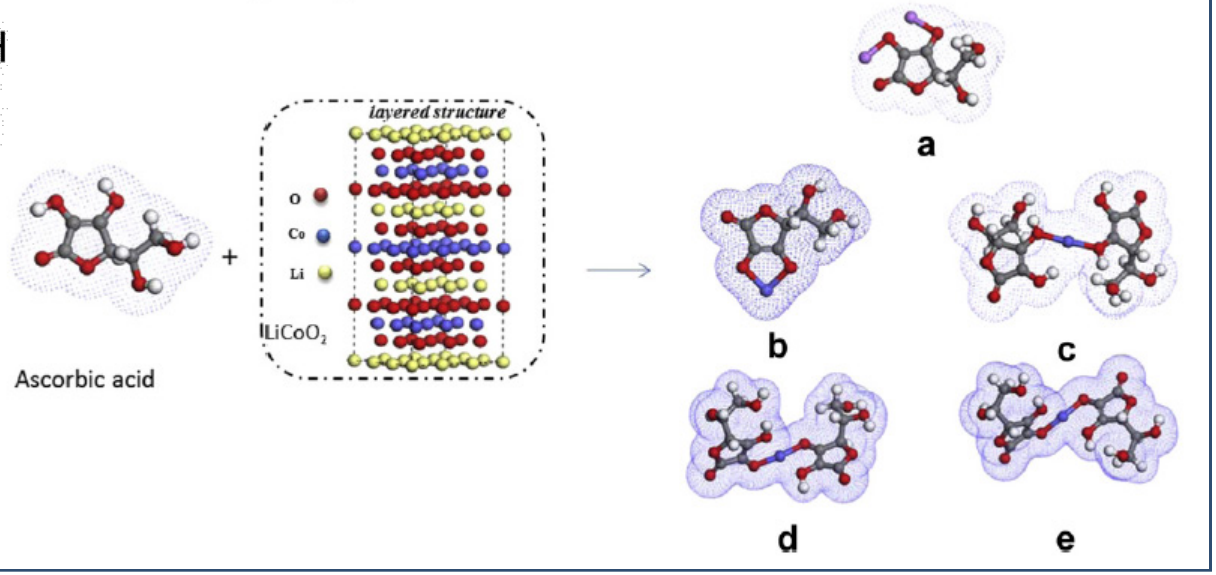


Fig Possible products of the leaching reaction of waste $LiCoO_2$ with ascorbic acid.

抗坏血酸对废旧电池中金属离子具有较高的离子浸出效率

High leaching efficiency can be achieved using ascorbic acid as leaching reagent and reducing agent for recovery of cobalt and lithium from spent LIBs.

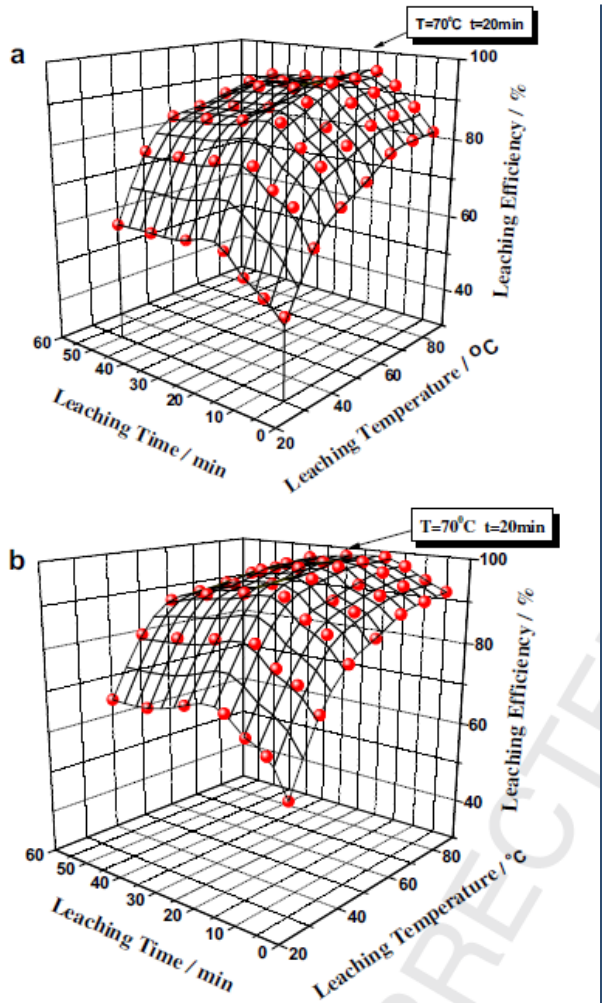


Fig. 8. Effect of temperature and time on the leaching efficiency of (a) cobalt and (b) lithium from waste $LiCoO_2$ ($t = 20$ min, $C = 1.25$ mol L^{-1}, $S/L = 25$ gL^{-1}, and agitation speed = 300 rpm).

以抗坏血酸为浸出剂和还原剂，钴和锂的浸取率分别为94.8%和98.5%，最佳浸出条件为：温度70℃，反应时间20min，抗坏血酸浓度为1.25M，固液比控制为25g/L。

Leaching efficiencies as high as 94.8% for Co and 98.5% for Li are achieved with a 1.25 mol/L ascorbic acid solution, leaching temperature of 70 C, leaching time of 20 min, and solid-to-liquid ratio of 25 g/L. This method is shown to offer an efficient way to recycle valuable materials from spent LIBs, and it can be scaled up for commercial application.

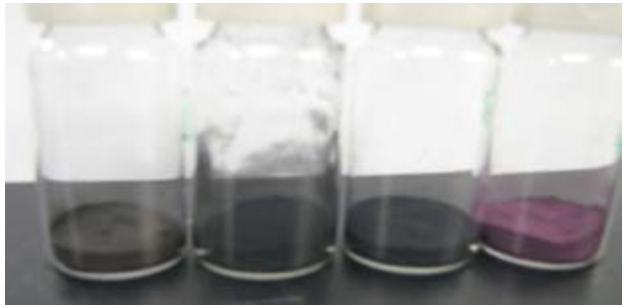
中美双方的合作工作成果已发表于Journal of Power Sources。

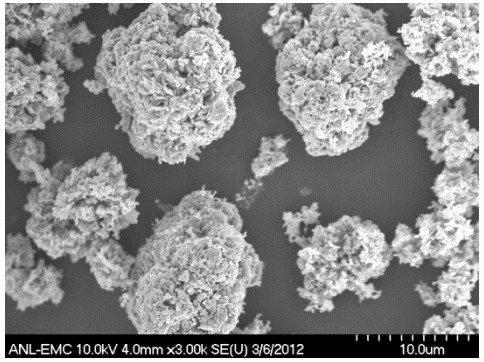
Li Li, Jun Lu , Yang Ren, Feng Wu *, Khalil Amine* *Journal of Power Sources*.

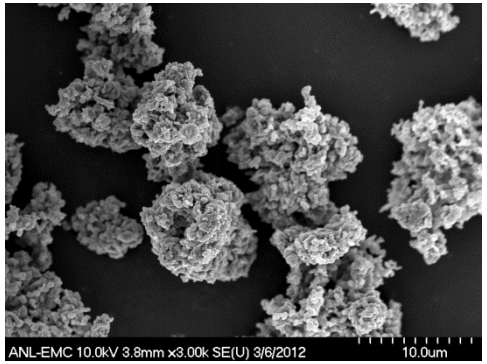
November 2012, Volume 218, 15. Pages 21–27

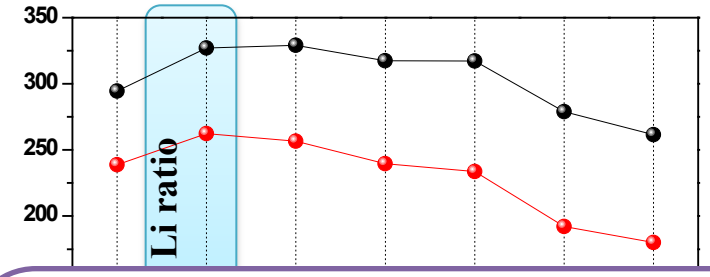
Synthesis and electrochemical characterization of $Li_xNi_{0.25}Mn_{0.75}O_2$ cathode material
富锂正极材料$Li_xNi_{0.25}Mn_{0.75}O_2$的合成与性能表征

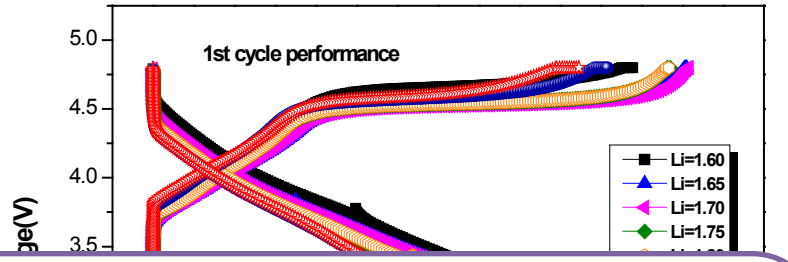
（Lithium Content Optimization 锂含量优化）









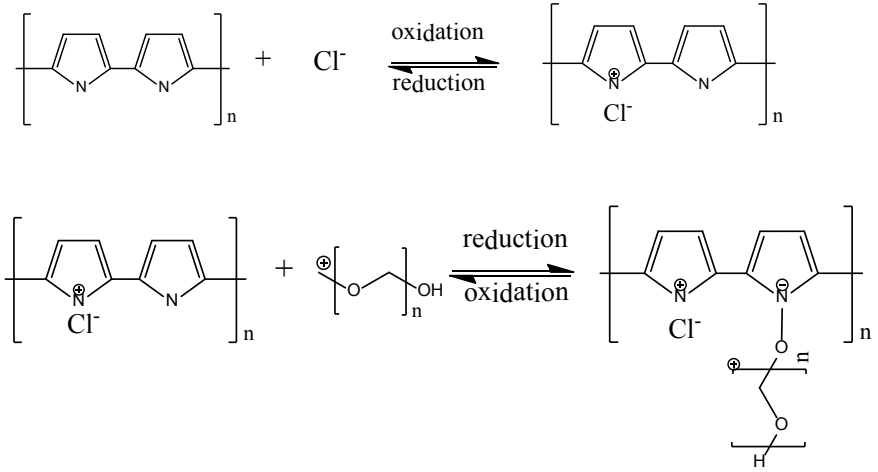


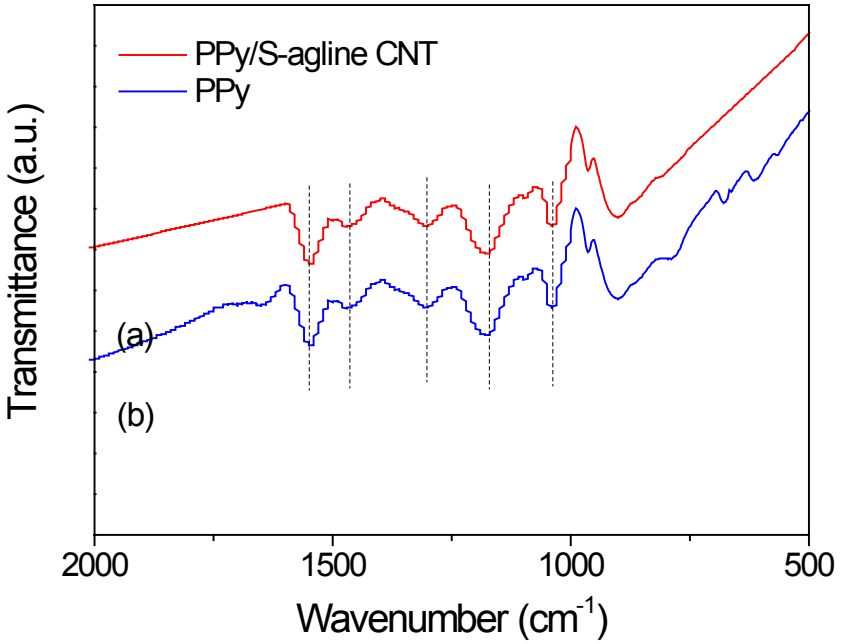
- 北理工以电池回收后的浸出液为原料，结合阿岗实验室的共沉淀技术制备新的正极材料，目前合成的材料表征及测试正在进行中。该过程有利于减少电池原材料的使用量、降低成本及减少环境污染。
- In BIT research group, new cathode materials are synthesized using the leaching solutions from spent LIBs by a co-precipitation method from Argonne. The materials testing are still in the process so far. It allows reduction of the amount of metal mining for the cathode materials, with reducing costs and harmful electrochemical waste.

锂硫电池与相关材料

PPy-PEG包覆硫/有序碳纳米管锂硫电池复合正极材料

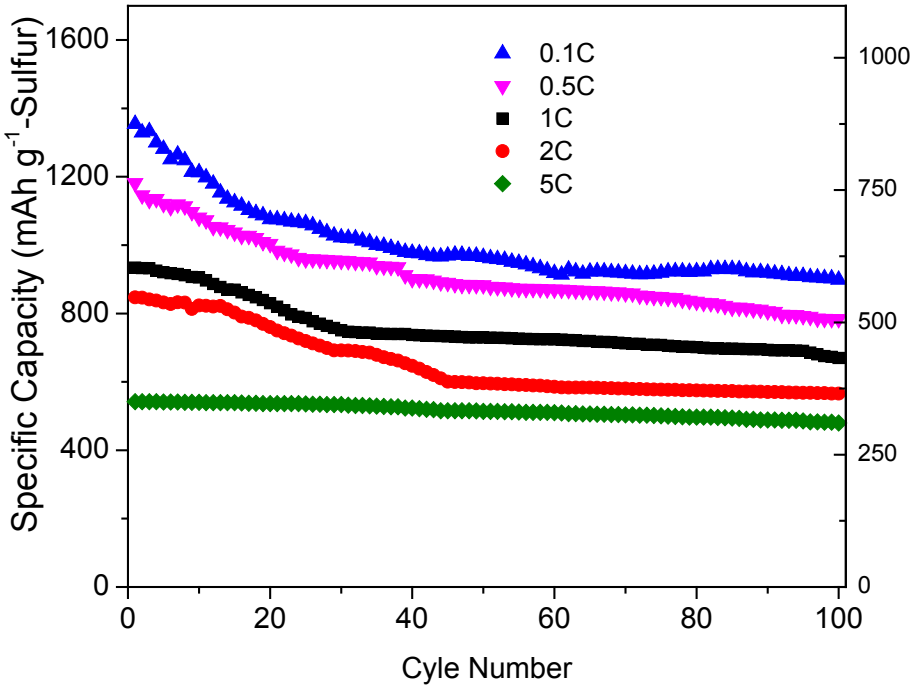
PPy-PEG Clothing Sulfur/Aligned Carbon Nanotube Cathode in Lithium Sulfur Battery

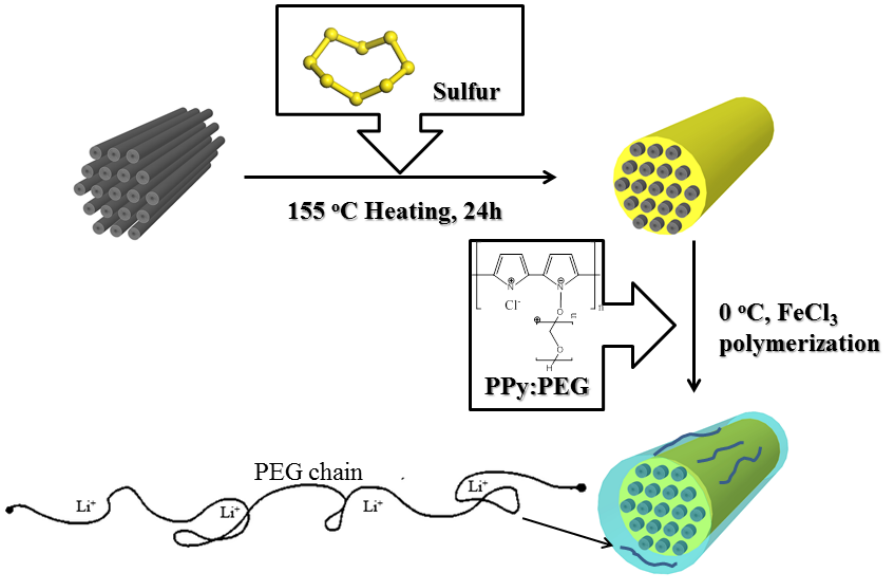




FT-IR confirms successful synthesis of PPy, doping PEG

红外光谱表明了正极材料中包含了掺杂PEG的导电PPy



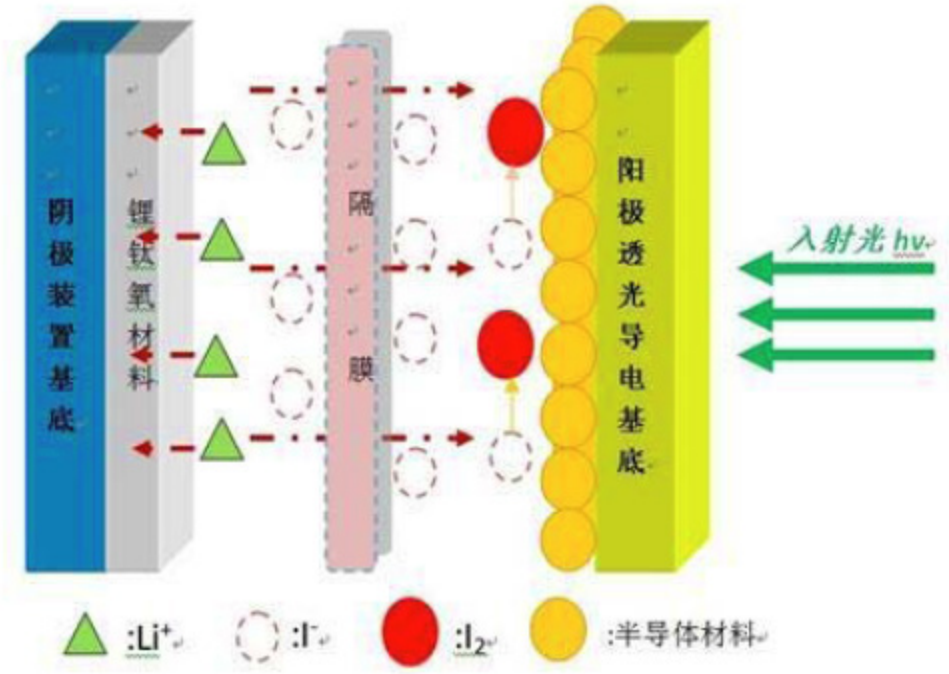


该包覆改性材料表现出良好的倍率性能和循环性能。5C（电流密度达到8A/g）时电池仍可正常工作，且放电容量可达542 mAh g^{-1}。

The rate performance of the polymer coating cathode is good as we reported before, After the PPy:PEG coating, the initial discharge capacity worked at 542 mAh g^{-1} in 5C(8A/g).

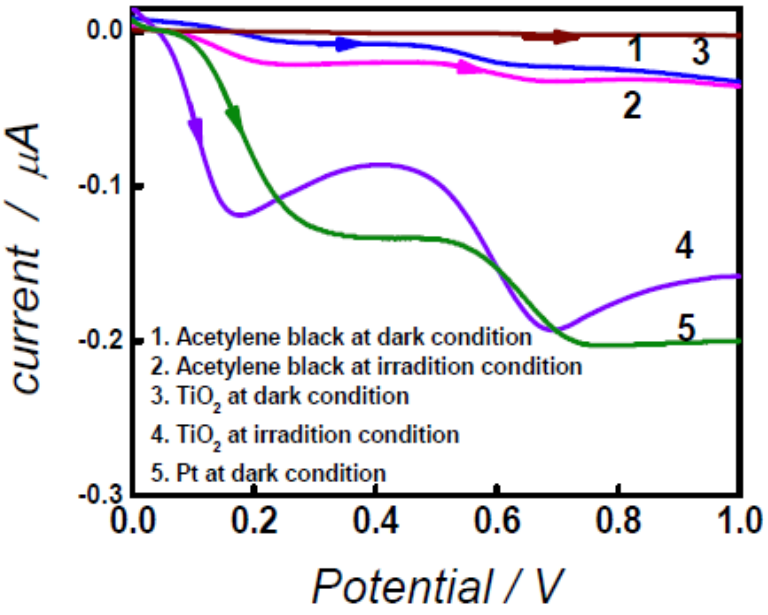
光辅助充电的Li-ion电池
Photo-assistant Rechargeable Li-ion battery

光辅助充电的Li-ion电池
Photo-assistant Rechargeable Li-ion battery



$Li_4Ti_5O_{12}$ | $LiClO_4$ (1mol L^{-1}) + PC + LiI (0.05molL^{-1}) |α|
$LiClO_4$ (1mol L^{-1}) + PC + LiI (0.05molL^{-1})| TiO_2/ITO

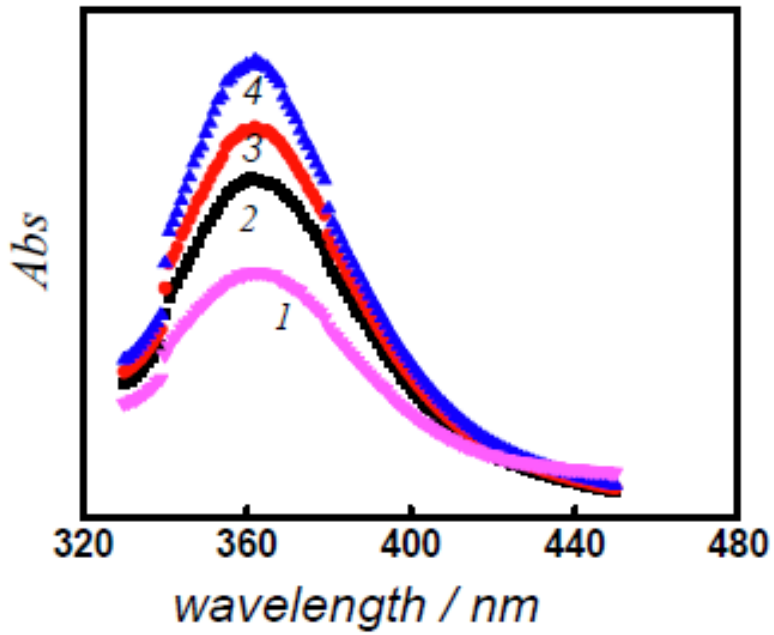
正极半电池光电电化学响应
The Cathode half cell photoelectrochemical response



光照条件下TiO_2材料表现出优良特性, 超过Pt和乙炔黑。

At the condition of irradiation TiO_2 exhibits excellent photo-electrochemical property and beyond the response of Pt and acetylene.

正极的充电效果——紫外可见响应
Charging effect of photo-positive electrode ——UV-vis response of charging products



在光照条件下随充电时间增加，正极半电池充电产物浓度增加

In positive half cell, the concentration of charging product increases with the increase of charging time at condition of irradiation.

光助充电反应机理
Photo-assistant Charging Mechanism of Electrodes and Full Cells

正极 $TiO_2 + 3h\nu \rightarrow 3TiO_2 + 3\ h^+ + 3e^-$

Cathode

$3h^+ + 3\ I^- \rightarrow 3/2\ I_2$

负极 $Li_4Ti_5O_{12} + 3Li^+ + 3\ e^- \rightarrow Li_7Ti_5O_{12}$

Anode

充电总反应 $3LiI + Li_4Ti_5O_{12} + 3h\nu \rightarrow 3/2\ I_2 + Li_7Ti_5O_{12}$

Whole cell

以上述机理制备的具有光辅助充电功能的Li-ion电池，有望解决由锂离子电池自放电引发的性能衰退问题。

The Li-ion battery using that mechanism would solve the performance fading problems caused by self-discharge issues in Li-ion battery.

关于中美动力电池合作交流的思考与展望
Perspective and Discussion for the Cooperation in Power Batteries between China-US

- 会议的模式还有待大家进一步探讨。
- 双方的交流还有待进一步广泛和深入。
- 双方的合作还有待进一步加强。

我衷心希望，我们的会议能像Larry先生的中国话一样越来越迷人，能像Amine博士的创意一样越来越活跃，能像杨晓青教授的诗句一样越来越精彩！

- Further discuss the organization ways of the workshop
- Extend communication
- Strengthen Cooperation

I hope from the botton of my heart, our workshop will get more attractive like Mr. Larry Johnson's spoken Chinese, more active like Dr. Khalil Amine's creativity and more brilliant like Prof. Xiaoqing Yang's poem.

Thank you for your attention !