结合中子散射技术研究下一代锂离子电池正极材料磷酸亚钴锂的性能改进及其内禀机制

Performance improving and its mechanism exploring for next-generation Li-ion batteries cathode material $LiCoPO_4$ combined with neutron scattering technologies

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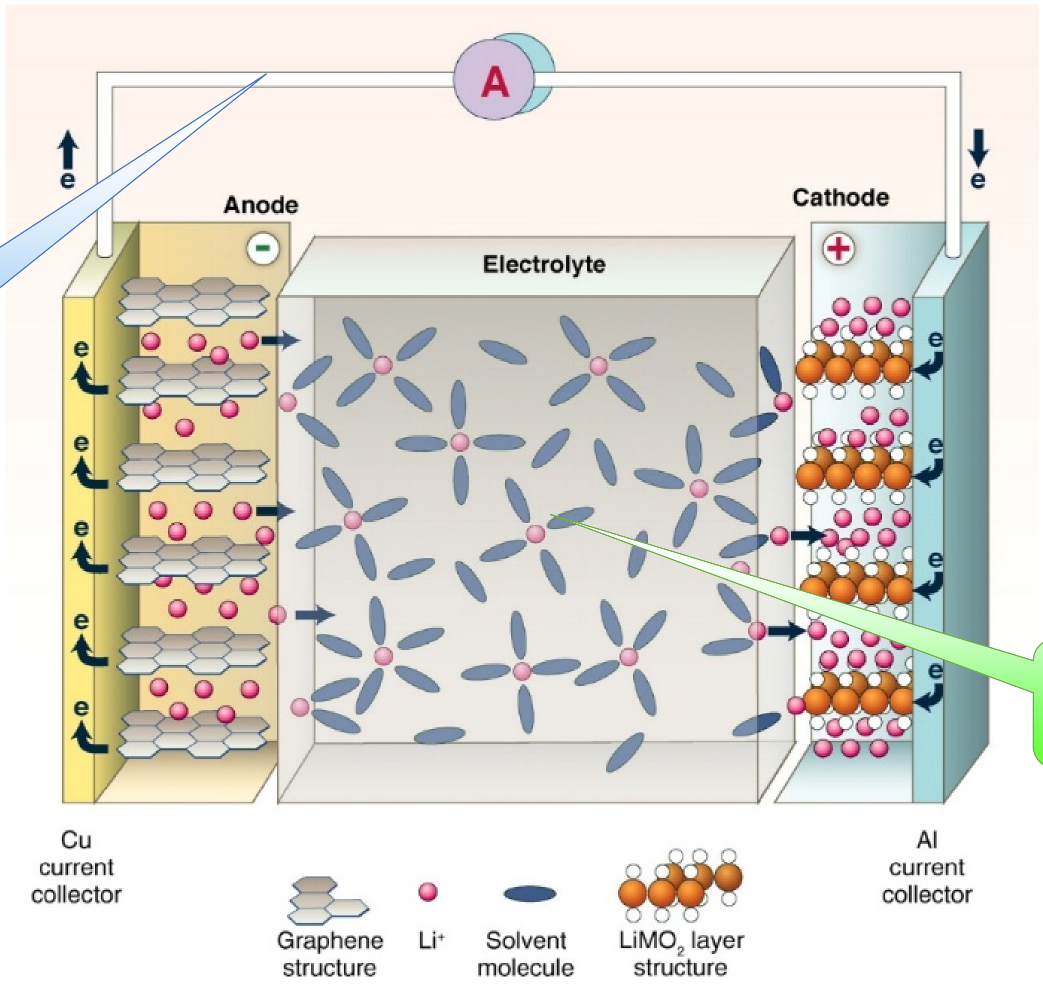
Advisors: 简宏希 王芳卫

2022.6.30 @ CSNS A1-104

Lithium-ion Battery



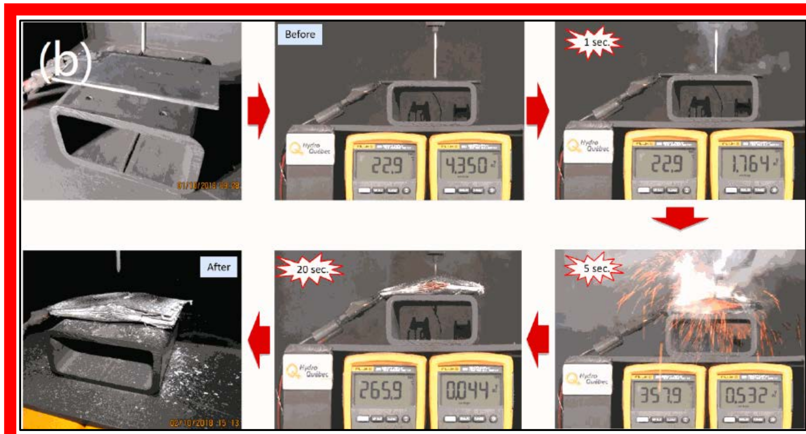
e- Path

Ion Path

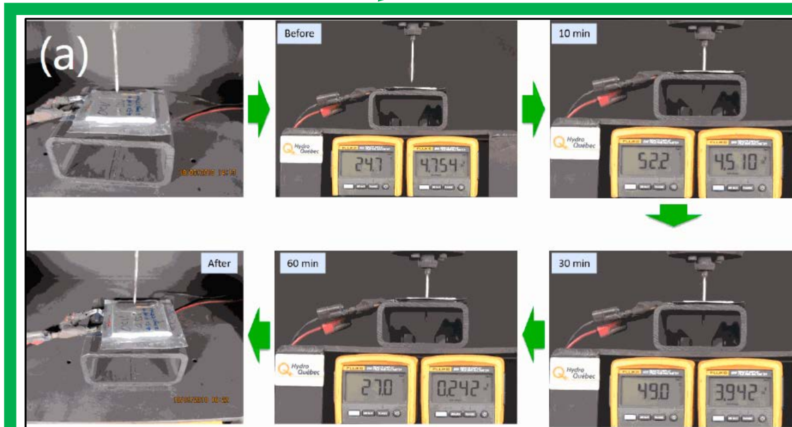
J.B. Goodenough, H.D. Abruna, M.V. Buchanan, Basic Research Needs for Electrical Energy Storage. Report of the Basic Energy Sciences Workshop on Electrical Energy Storage, April 2-4, 2007, United States, 2007.

$LiCoPO_4$ (LCP)

正极材料	$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$	$LiFePO_4$	$LiCoPO_4$
理论容量 (mA h g^{-1})	277.8*0.7=194.5	169.9	166.6
对锂电位 (V)	3.6	3.45	4.8
理论能量密度 (W h kg^{-1})	700	586	800
热稳定性	差	优秀	优秀



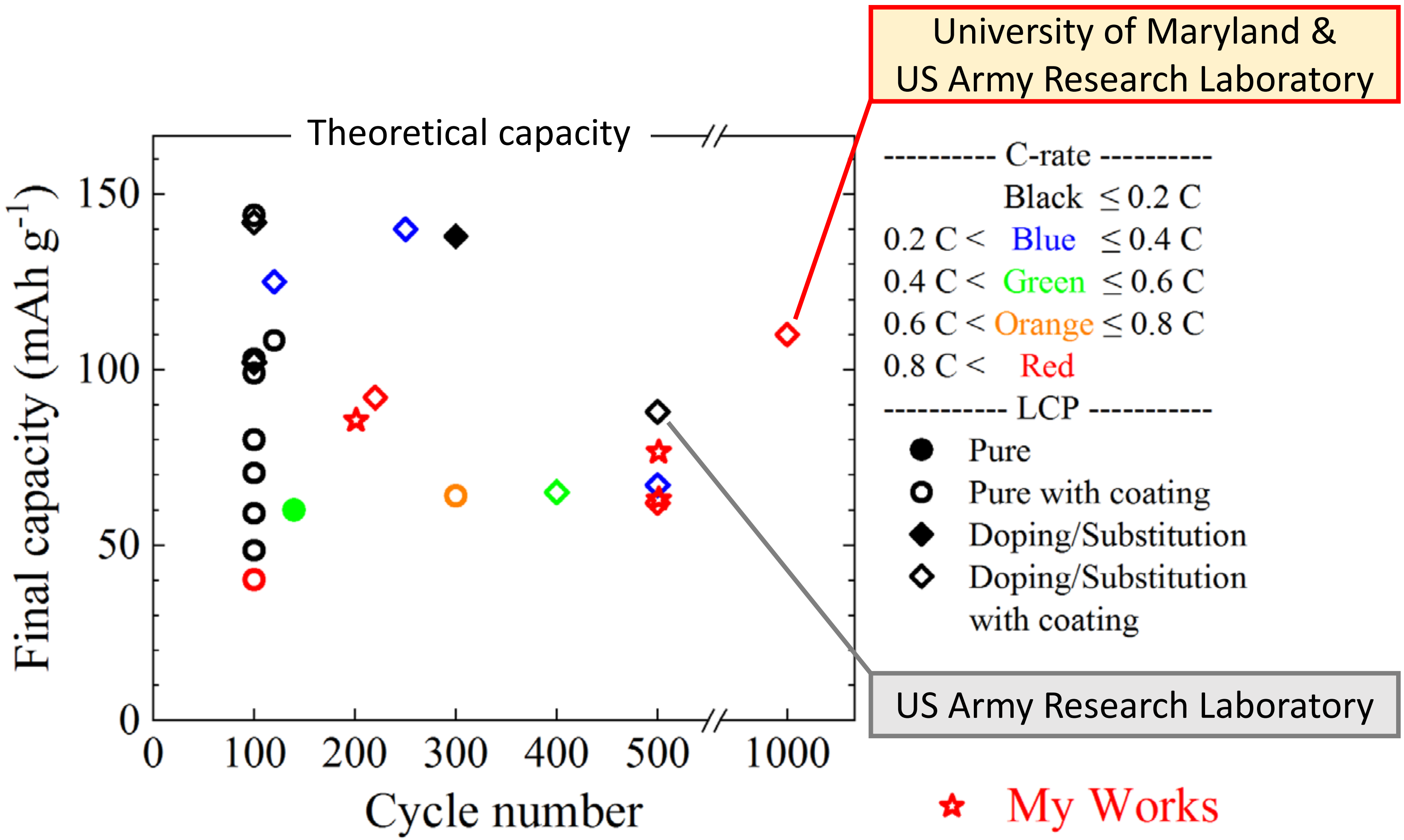
iPhone cell



LCP cell

C.-X. Zu, H. Li, Thermodynamic analysis on energy densities of batteries, Energy Environ. Sci., 4 (2011) 2614-2624.
D. Liu, C. Kim, A. Perea, D. Joël, W. Zhu, S. Collin-Martin, A. Forand, M. Dontigny, C. Gagnon, H. Demers, S. Delp, J. Allen, R. Jow, K. Zaghib, High-Voltage Lithium-Ion Battery Using Substituted LiCoPO4: Electrochemical and Safety Performance of 1.2 Ah Pouch Cell, Materials, 13 (2020).

Practical Performance

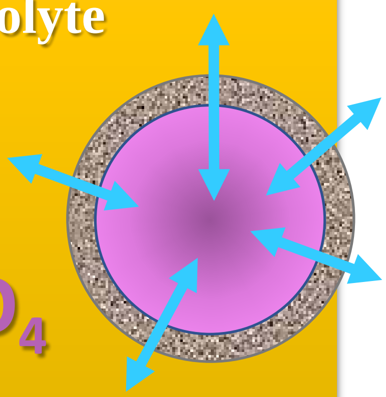


Strategies for Improving Performance

Problems

- **Poor conductivity: $<10^{-9}$ S cm^{-1}**
- **Li-Co anti-site defect**
- **~4.8 V—— Electrolyte**
- **Cobalt**

$LiCoPO_4$



Strategies

(1) Shortening lithium pathway

Sol-gel, Hydrothermal, Co-precipitation, Spray Pyrolysis, ……

(2) Ion doping (Intrinsically!)

Metal Ion, anion； Li-site, Co-site;

(3) Surface modification

Carbon, Ionic Conductor, Blend Coating;

(4) External factors

Electrolyte: additives, solutes, solvents; Separator；

(5) Application Scenarios

Research Plan

1. 厘清LCP在脱/嵌锂过程中锂离子迁移和扩散的基本机制

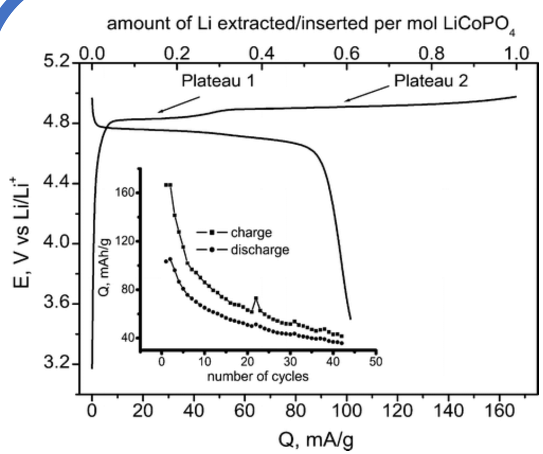
2. 量化“钴锂反位缺陷”在充放电过程中对LCP循环寿命的影响权重

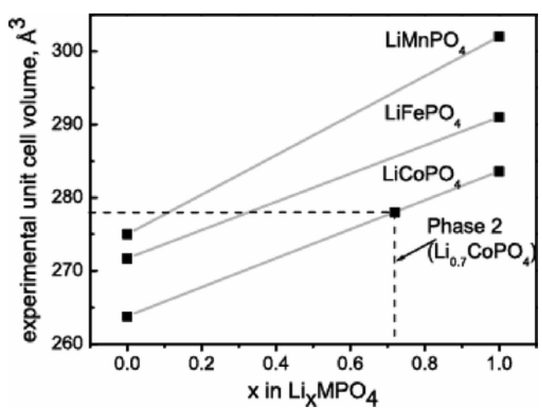
3. 从晶体结构入手为LCP元素掺杂最优比例寻求理论依据

4. LCP脱锂相高熵固溶化的前瞻探索

1. 厘清LCP在脱/嵌锂过程中锂离子迁移和扩散的基本机制

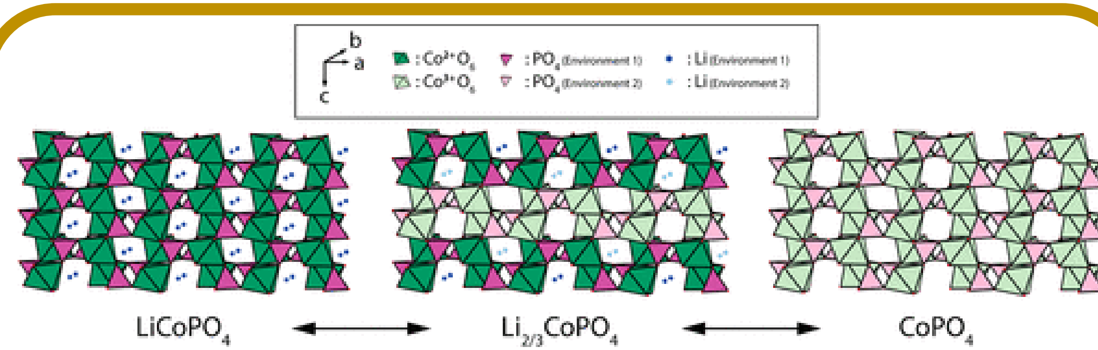
$Li_{0.7}CoPO_4$



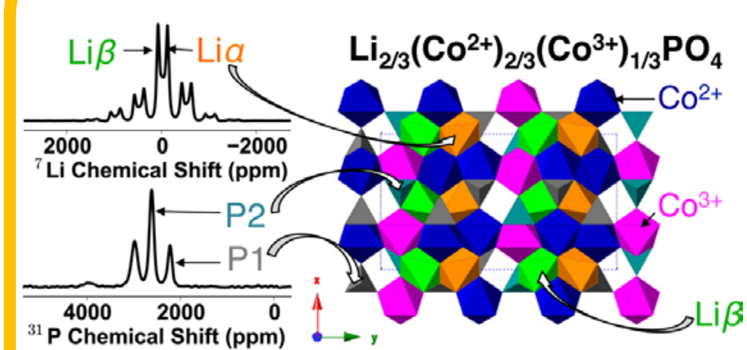


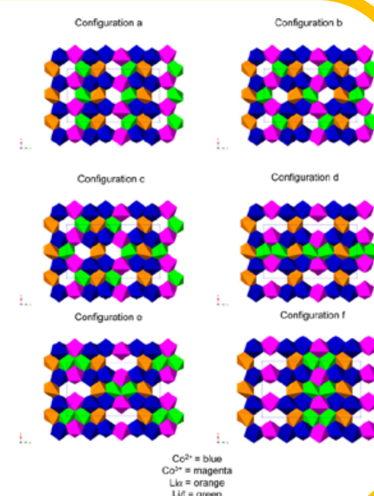
Chem. Mater. **2007**, *19*, 908–915

$Li_{2/3}CoPO_4$



J. Phys. Chem. C 2014, 118, 17279-17290



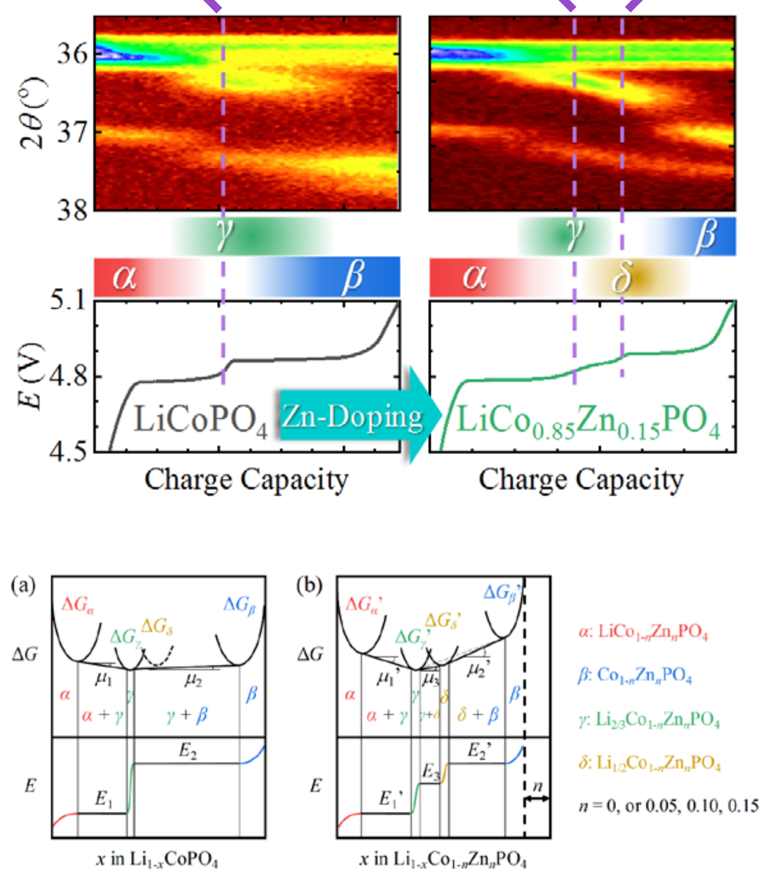


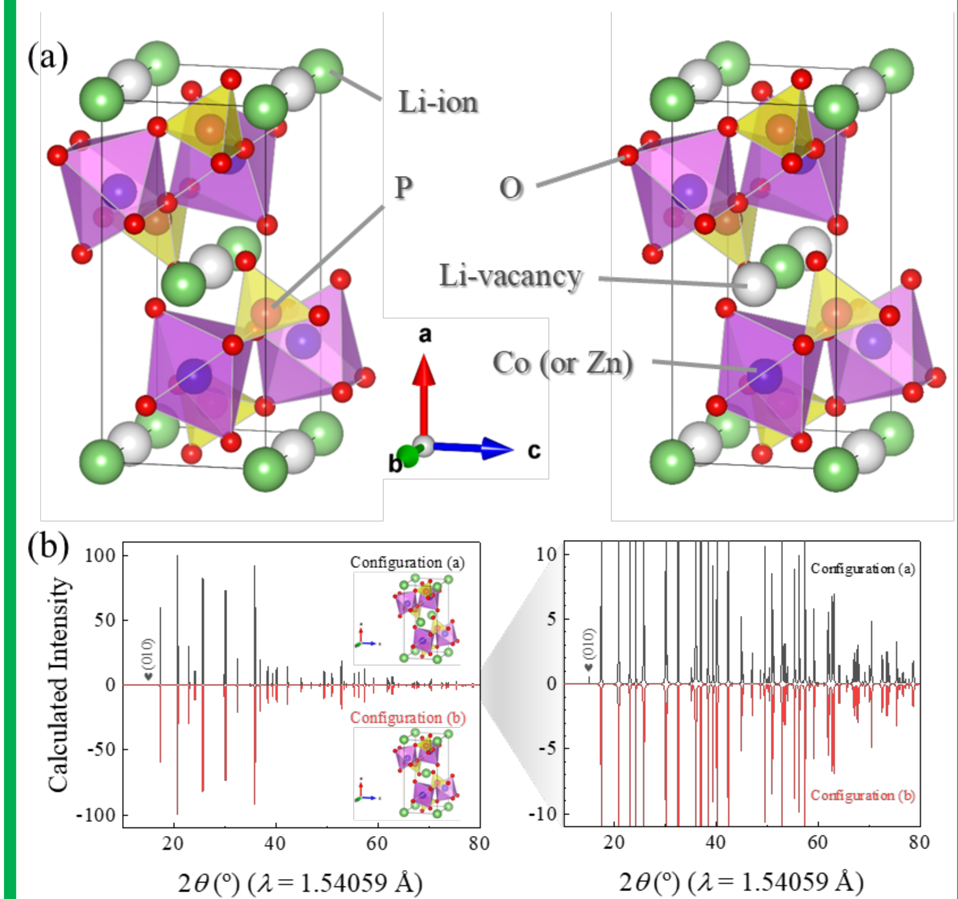
Chem. Mater. 2014, 26, 6193-6205

1. 厘清LCP在脱/嵌锂过程中锂离子迁移和扩散的基本机制

$Li_{2/3}Co_{1-x}Zn_xPO_4$

$Li_{1/2}Co_{1-x}Zn_xPO_4$





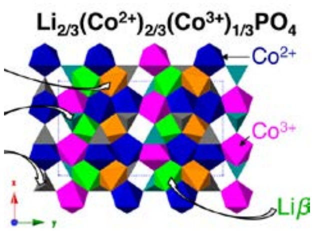
1. 厘清LCP在脱/嵌锂过程中锂离子迁移和扩散的基本机制

$LiCo_{1-x}M_xPO_4$

Chemical delithiation

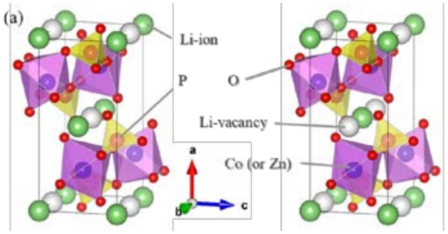
$Li_{2/3}CoPO_4$

$Li_{1/2}Co_{1-x}Zn_xPO_4$



Neutron Diffraction

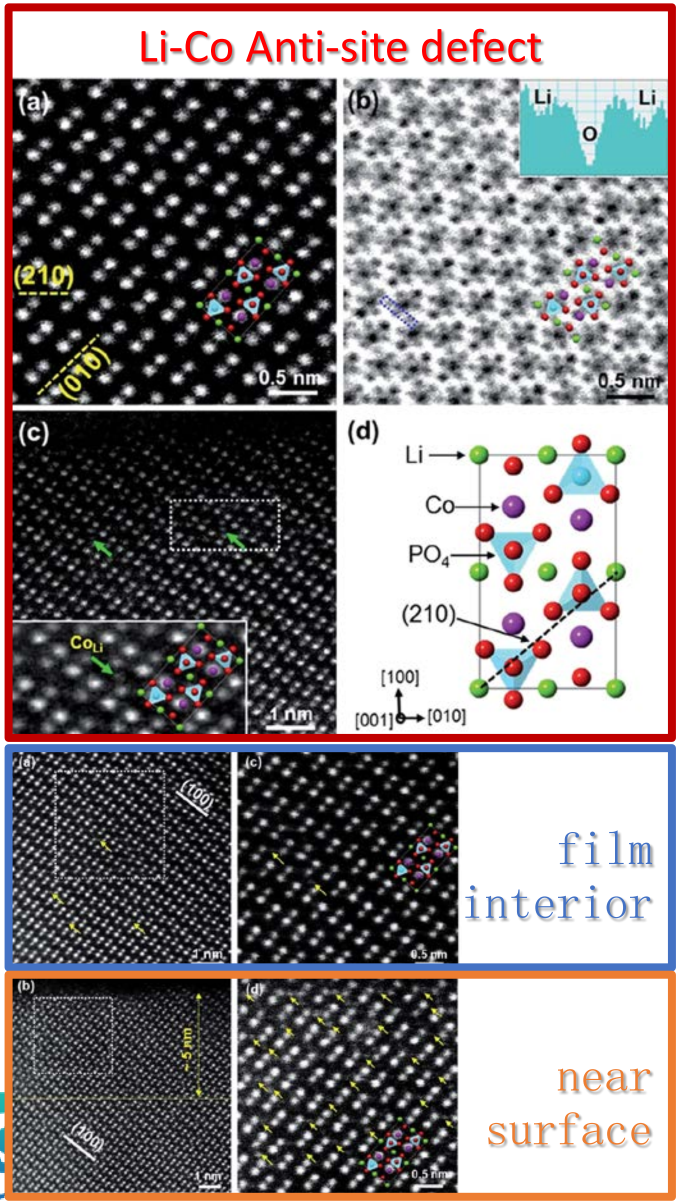
Rietveld Refinement



Crystalline Configuration of the Intermediate Phases

Mechanism of Delithiation/Lithiation

2. 量化“钴锂反位缺陷”在充放电过程中对LCP循环寿命的影响权重



$LiCoPO_4$

↓

Long-term Charge/Discharge Cycling

↓

Neutron Diffraction

↓

Rietveld Refinement

↓

Quantify the percentage of
Li-Co Anti-site defect

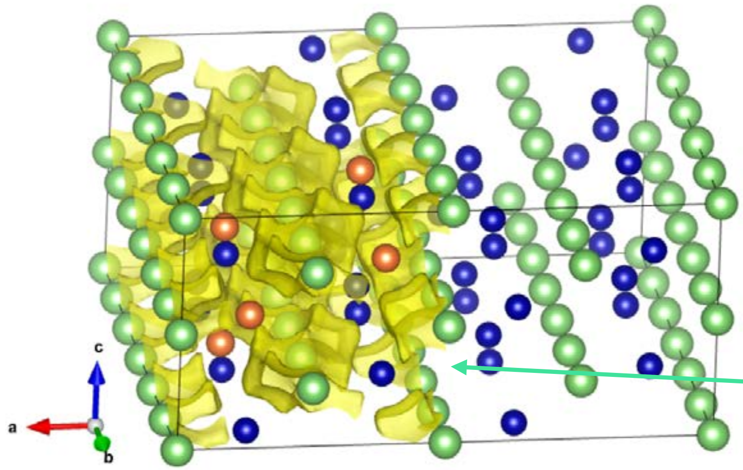
J. Mater. Chem. A, 2017, 5, 9329 - 9338

3. 从晶体结构入手为LCP元素掺杂最优比例寻求理论依据

Doping concentration → Electrochemical performance

↓

☑ How
☒ Why



Doping Concentration

→ Supercell Calculation ↔ PDF

→ Element-Rich Cluster

→ Affecting the Tunnel for Li-ion

→ BVS/BVEL Calculation ↔ Electrochemical Experiment

→ How & Why

SNS

4. LCP脱锂相高熵固溶化的前瞻探索

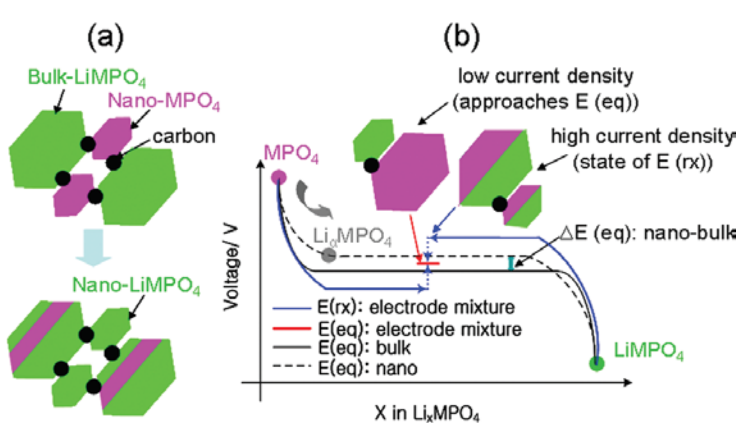
本计划

多元混合 → 混合熵S↑ → $S\Delta T$项主导ΔG

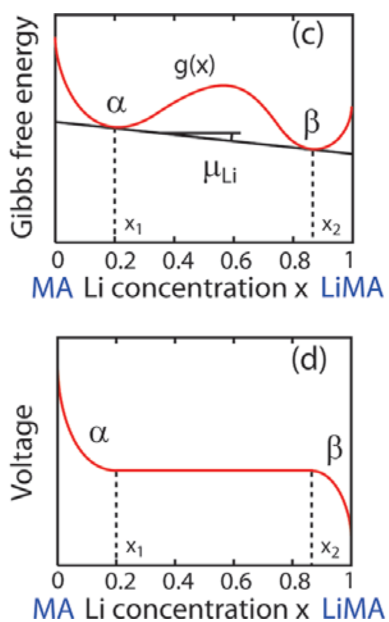
$$\Delta G = \gamma\Delta A - S\Delta T + \varepsilon X + kT[X\ln X + (1-X)\ln(1-X)]$$

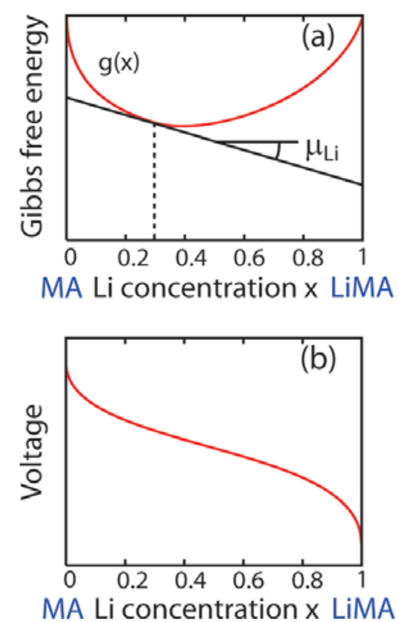
前人工作

- 粒径↓，比表面能↑，则$\gamma\Delta A$项主导ΔG
- 温度T↑，则$S\Delta T$项主导ΔG
- 脱锂比例X（$0 \le X \le 1$）影响项



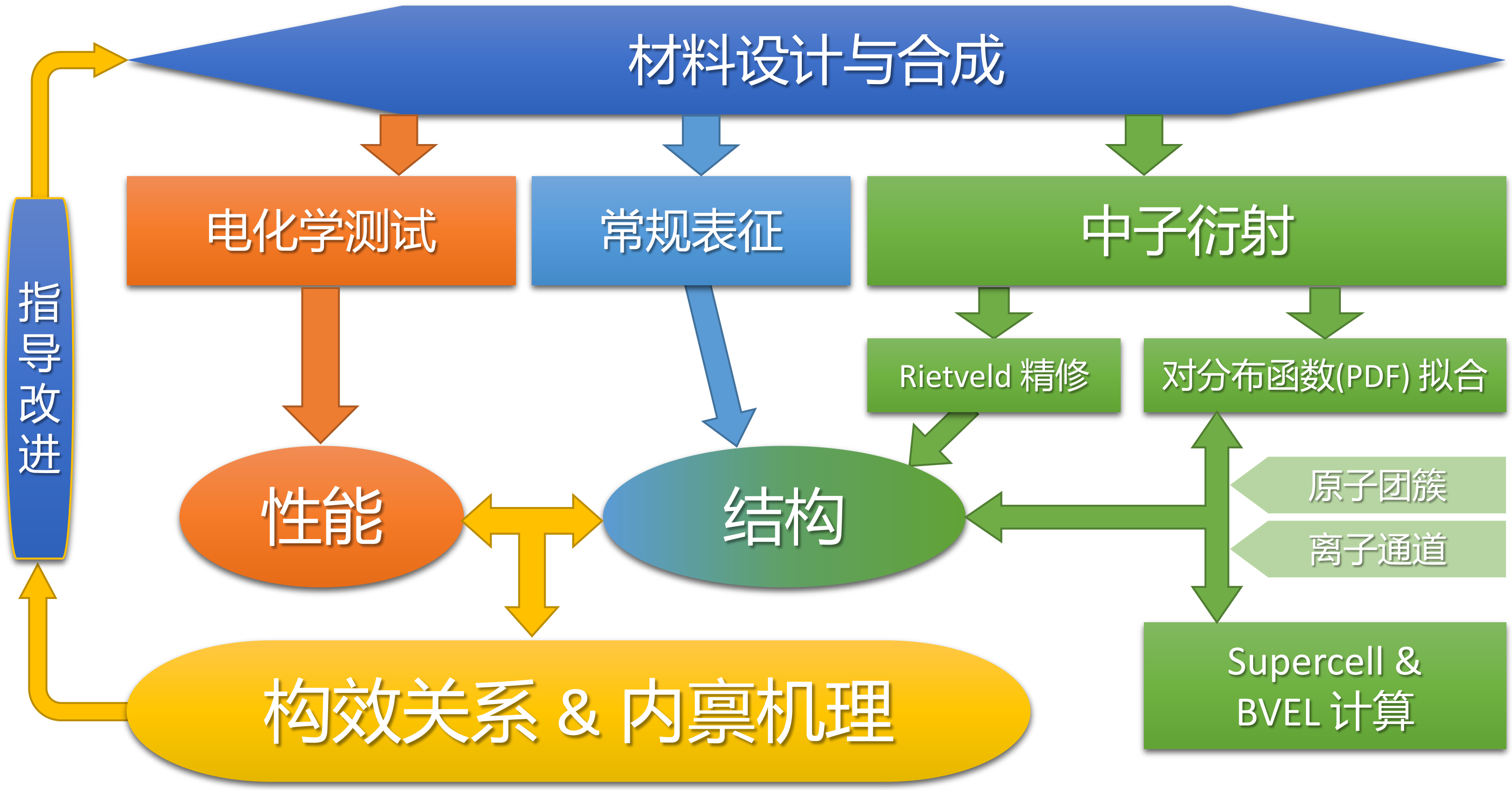
JACS. 2009, *131*, 6044–6045





ACCOUNTS OF CHEMICAL RESEARCH ' 1216 - 1225 ' 2013

Roadmap


材料设计与合成
电化学测试
常规表征
中子衍射
Rietveld 精修
对分布函数(PDF) 拟合
指导改进
性能
结构
原子团簇
离子通道
Supercell &
BVEL 计算
构效关系 & 内禀机理

Planning Phase

阶段内容	2022				2023				24	成果产出风险指数	预期发表论文篇数	预期申请专利个数
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1			
初期研究平台构建与前期实验验证										★☆☆☆☆	0	0
LCP脱/嵌锂中间相结构的研究										★★☆☆☆	1~2	0
长循环充放电钴锂反位缺陷的研究										★★☆☆☆	1~2	0
不同掺杂晶体结构的计算和实验验证										★★★☆☆	1~3	1~2
LCP脱锂相高熵固溶化的前瞻探索										★★★★★	0~2	0~2
合　　计											3~9	1~4

Construction Project

中子电化学平台

The Electrochemical Platform for Neutron Source

EPNS

建设
软包电池
和
圆柱电池
实验线

开发
中子透明
电池封装
部件

开发
新型
无氢隔膜

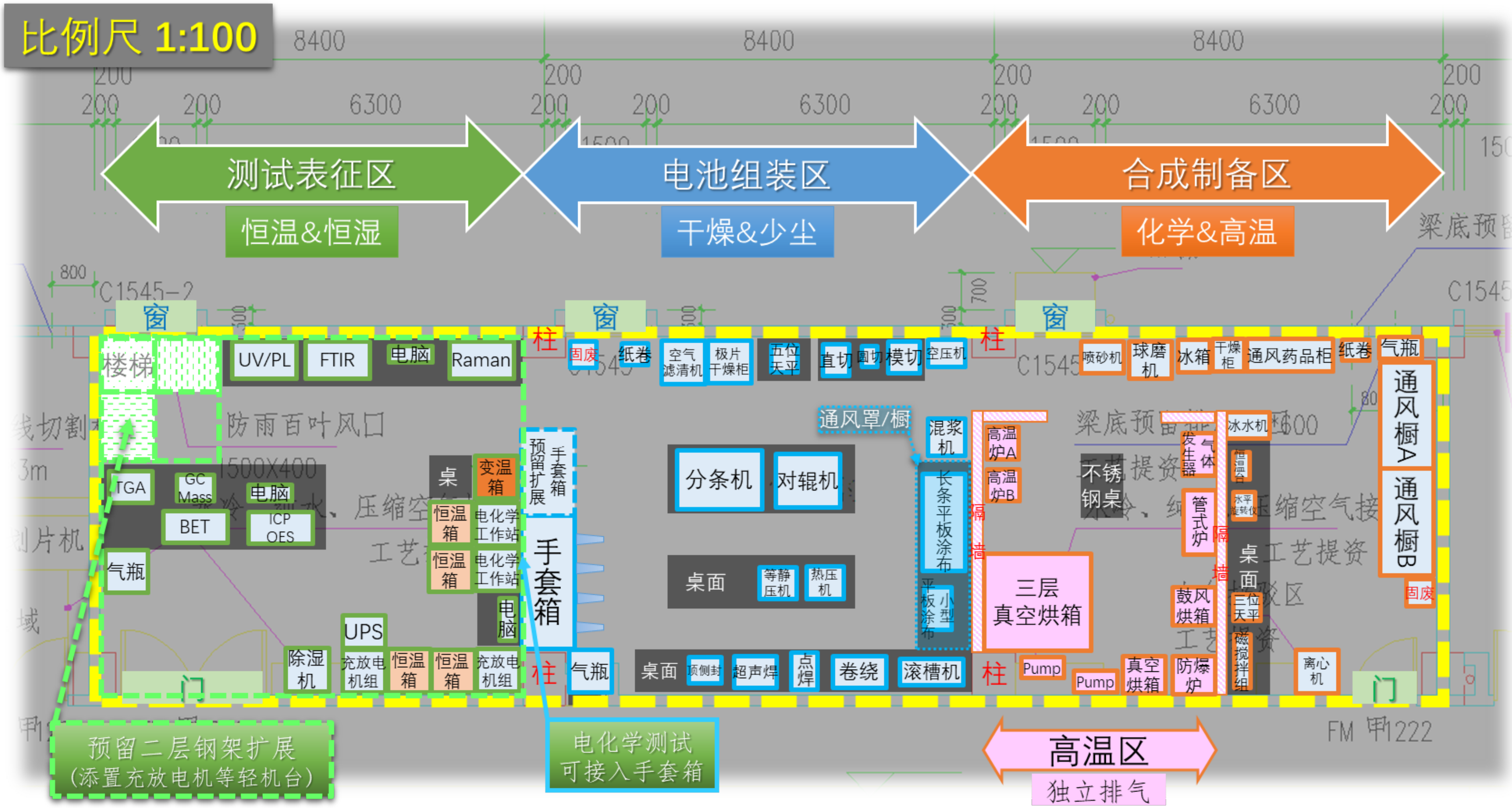
优化
厚电极
加工方法

开发
氘型
电解质

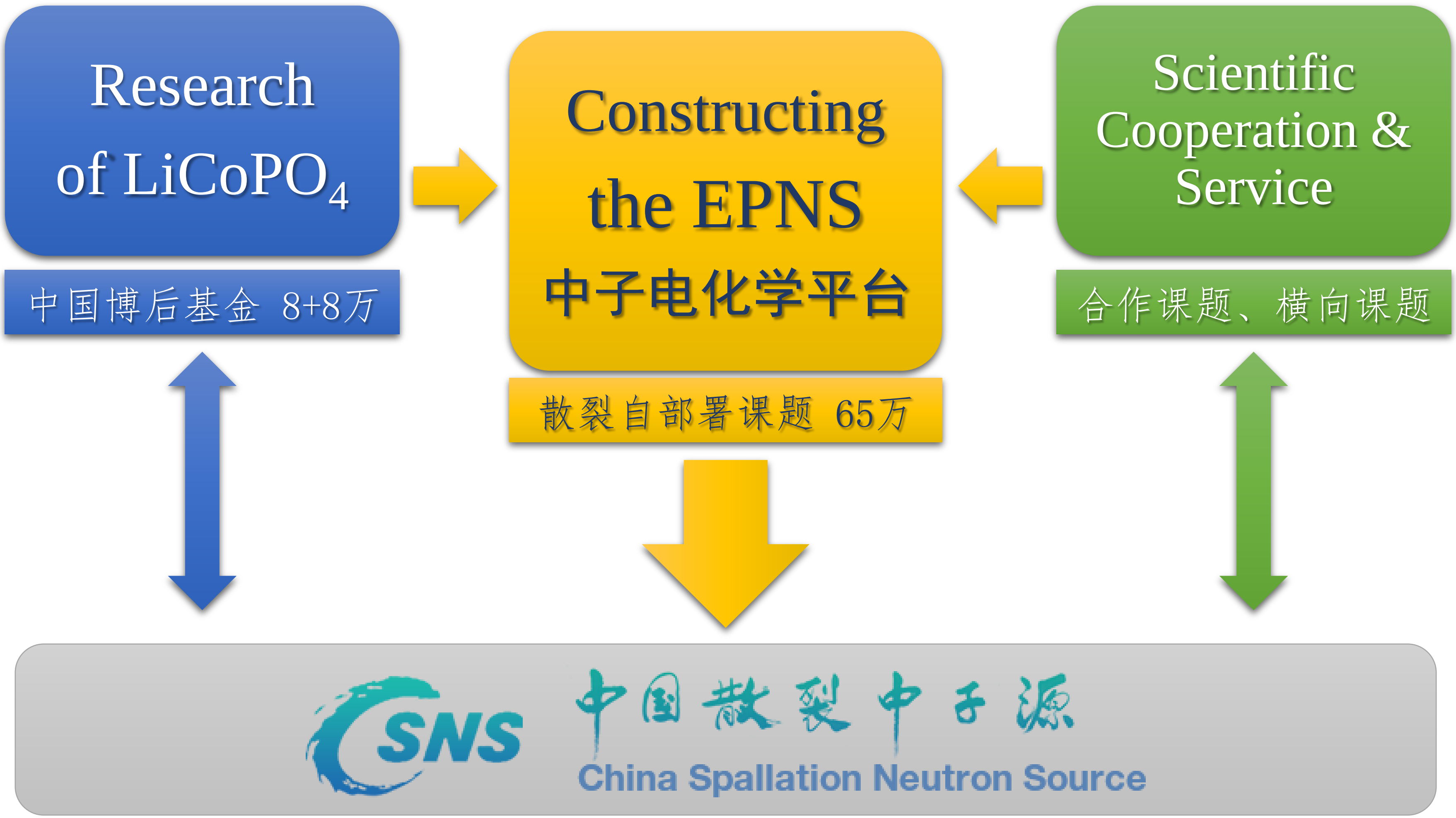
…

SNS

Construction Project



Conclusion


Research of $LiCoPO_4$
中国博后基金 8+8万
Constructing the EPNS
中子电化学平台
散裂自部署课题 65万
Scientific Cooperation & Service
合作课题、横向课题
中国散裂中子源
China Spallation Neutron Source


Thank you~