

Li-ion Batteries: Layered Cathodes & Rechargeable Li Anodes

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Contents

- How to Obtain High specific Energy Li-ion Battery

NMC-Li Battery is one of the most promising systems

- Why Single Crystalline Cathode?

High cyclic stability, high packing density &…

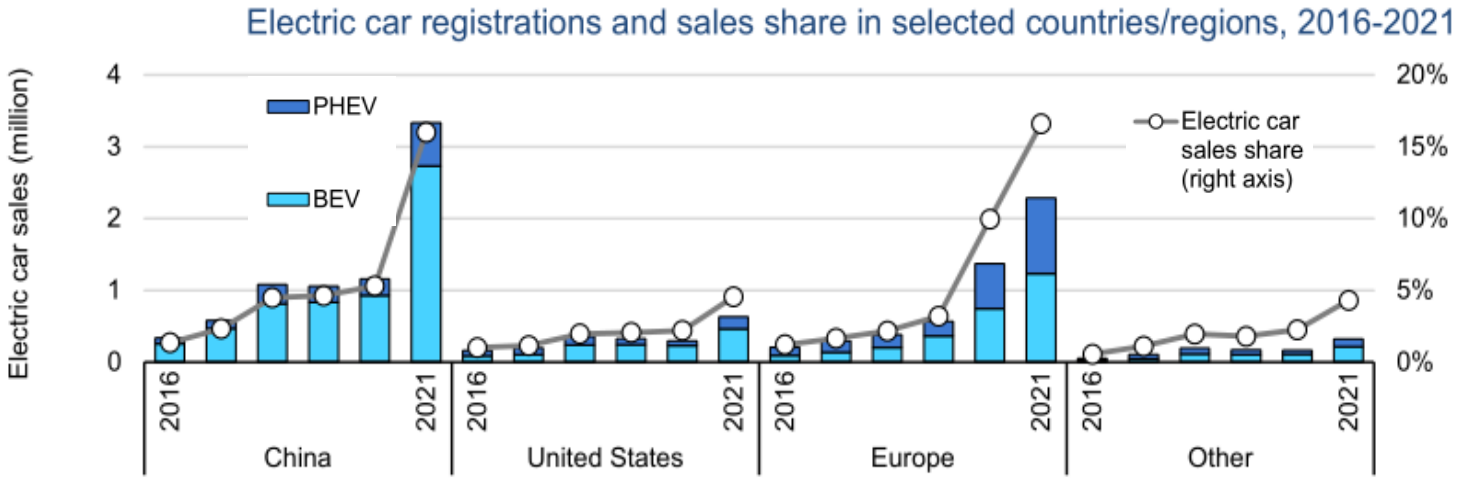
- How to make Li anode more rechargeable ?

Less dead Li & Stable/flexible SEI with good morphology

- Conclusion & Outlook

Rapid Development of Li-ion Batteries in Last 30 Years





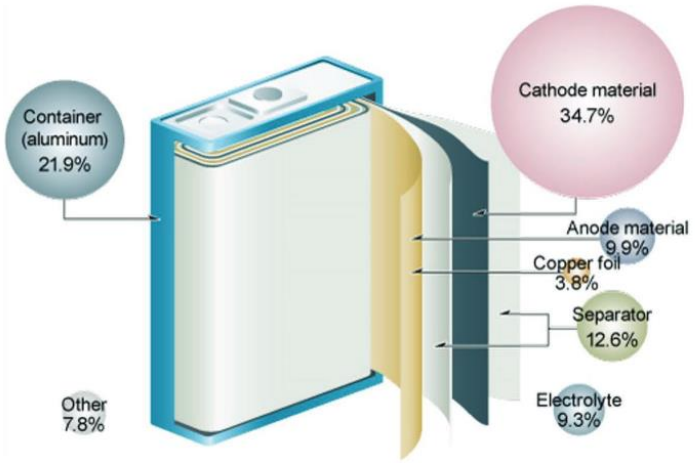
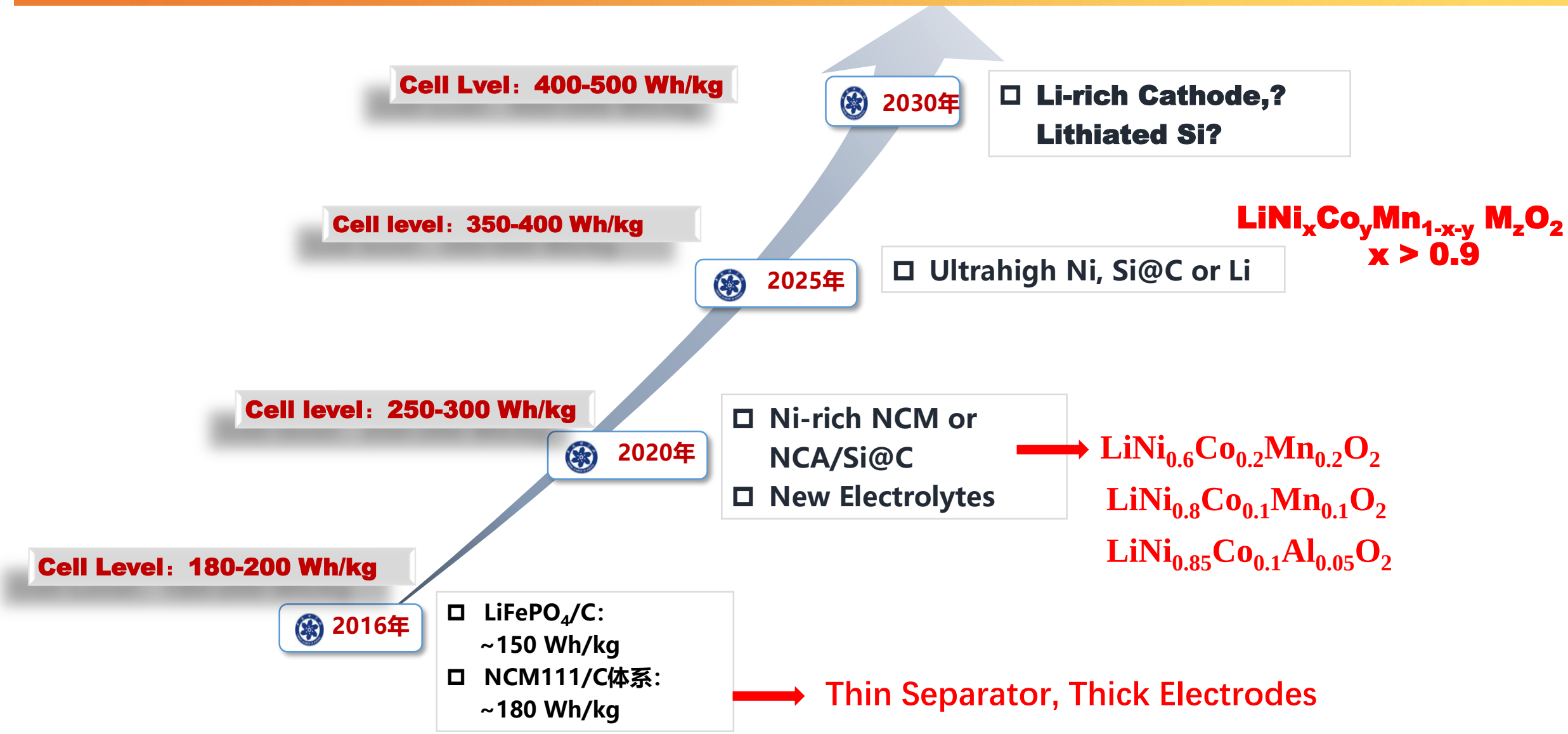


Table 1
Comparison of the properties of the current cathode materials in LIBs.

Material	$LiCoO_2$	$LiNiO_2$	$LiNi_{0.8}Co_{0.2}O_2$	$LiMn_2O_4$	$LiFePO_4$	NCM/NCA
Research time (year)	1980	1985	1992	1983	1997	1999
Theoretic/experimental capacity (mAh g^{-1})	274/140–155	275/≥150	275/≥170	148/100–120	170/90–165	~280/155–220
Voltage plateau (V vs. Li/Li^+)	3.8	3.8	3.8	4.1	3.4	3.7
Cycling stability (time)	≥500	–	–	≥500	≥2000	≥800
Tap density (g cm^{-3})	2.8–3.0	2.4–2.6	–	2.2–2.4	1.0–1.7	2.0–3.0
Cost	High	Medium	Medium	Low	Low	Medium
Safety	Low	Low	Medium	Medium	High	Medium
Toxicity	High	Medium	Medium	Low	Low	Medium
Synthesis	Easy	Difficult	Difficult	Easy	Medium	Medium
LIB application	Portable devices	Portable devices	EV	EV	EV, massive energy storage	Portable devices, EV

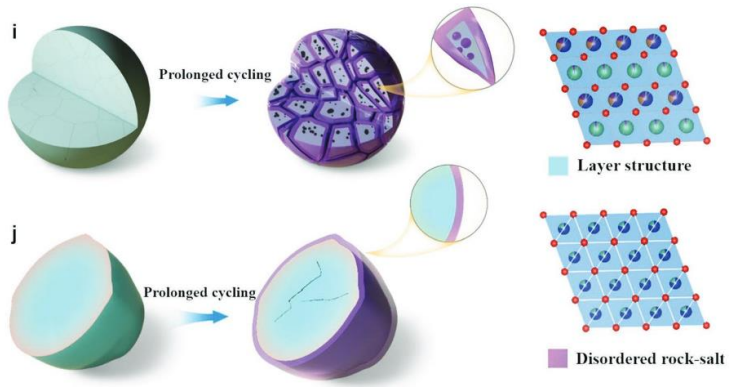
Global EV Outlook 2022, IEA, Paris *Adv. Energy Materials, 2019, 9(27).* *Progress in Materials Science, 2020,111:100655.*

Roadmap for EV battery in China （2016-2030）

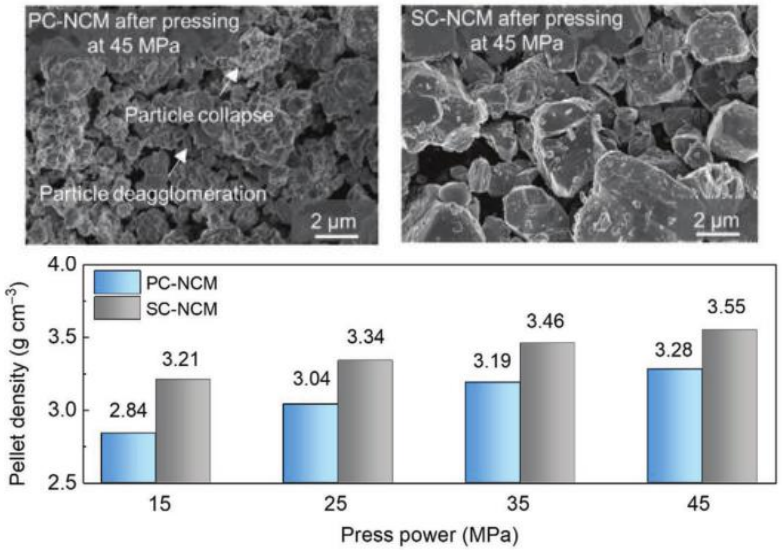


State-of-Art of the Single Crystalline NMC Cathodes

Advantages

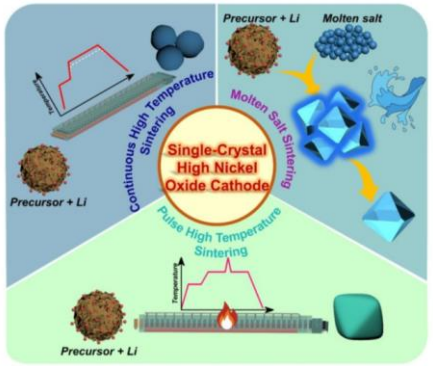


Long cyclic life, Less Cracks

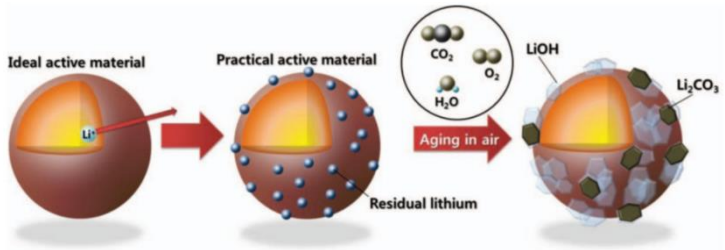


Good mechanical properties、High Packing density

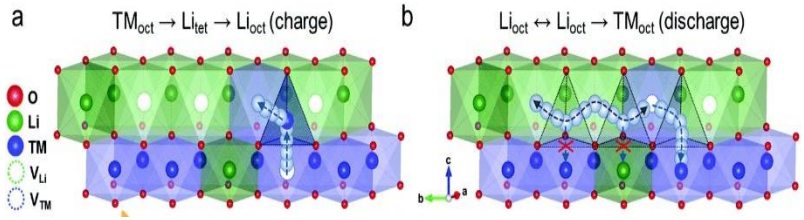
Shortages



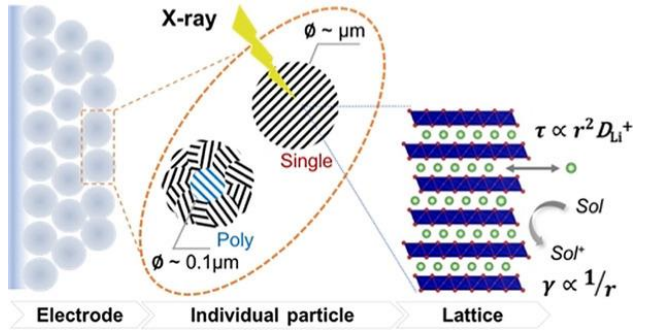
Quite Complex Synthesis



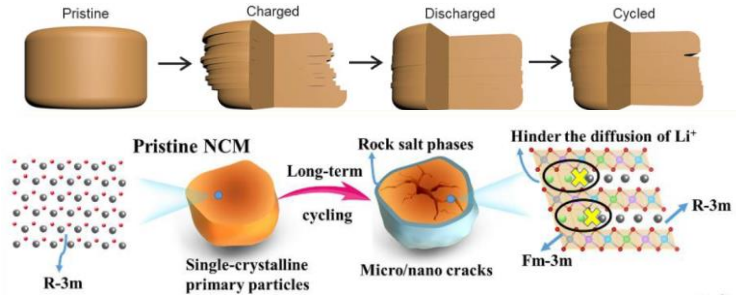
Alkaline-rich Surface



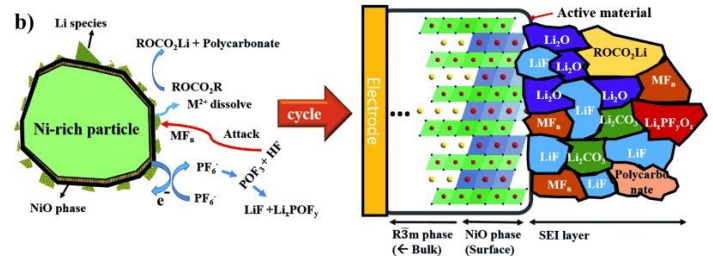
Cation Mixing



Long Li^+ Diffusion Path



Latice Sliding & Internal Crack



Interfacial Reactions

Small 2022, 18, 2107357

Adv. Mater. 2020, 32, 2003040

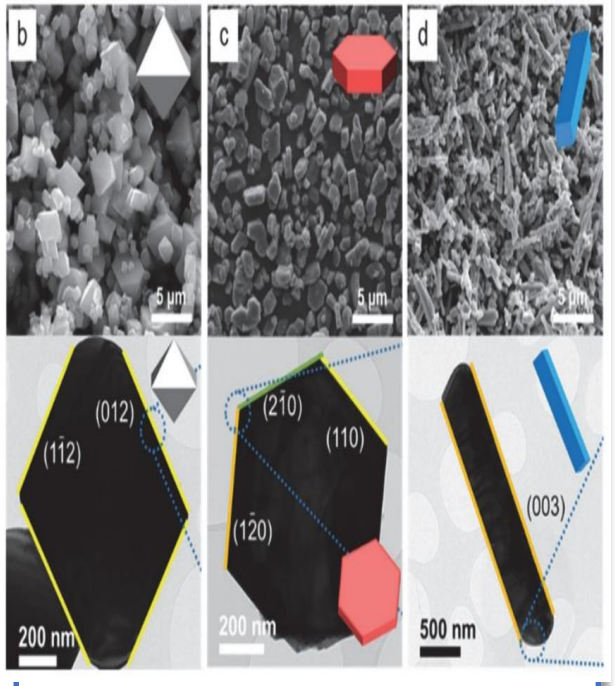
J Mater Sci (2020) 55:2913–2922

Science 2020, 370, 1313

ACS Energy Lett. 2021, 6, 2726−2734

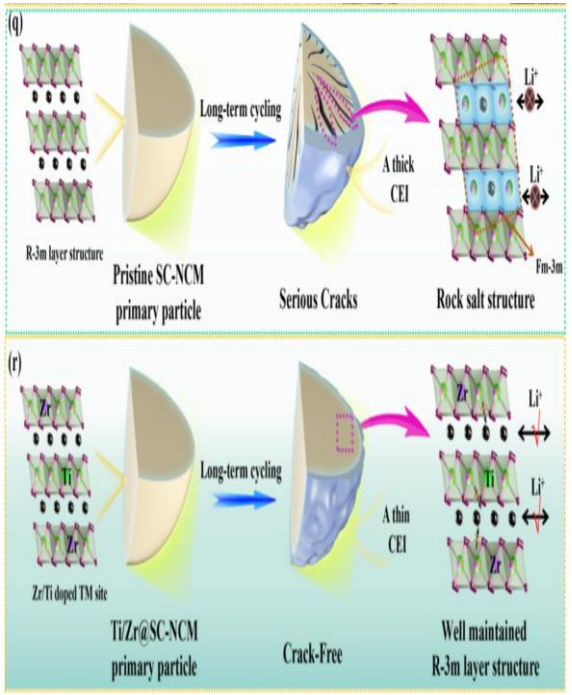
Performance Enhancing Strategy for SC NMC Cathode

Synthesis Optimization



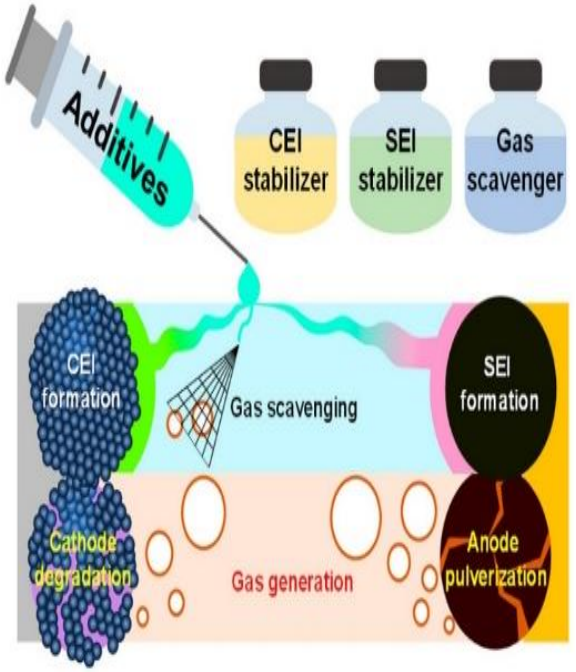
Size , Morphology/ Crystalline Facet Control by optimizing flux and temperature

Doping



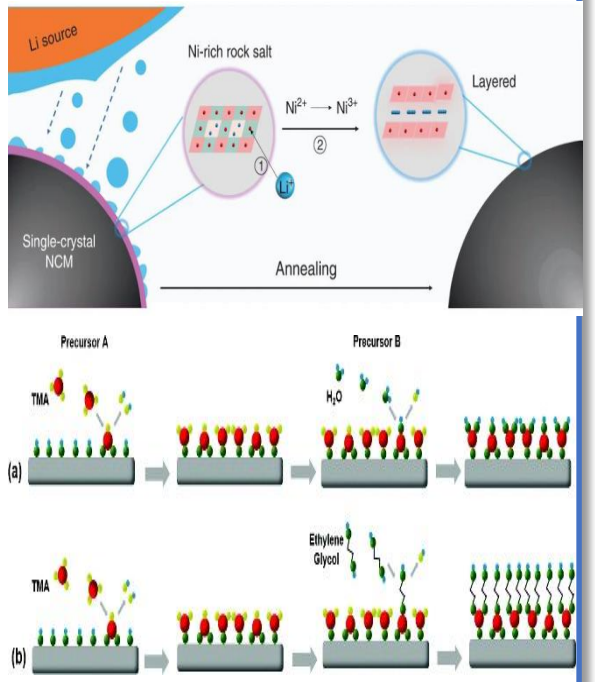
Choices of Doping element, Multiple doping and Electrochemical-mechanical Coupling

Electrolyte Addtives



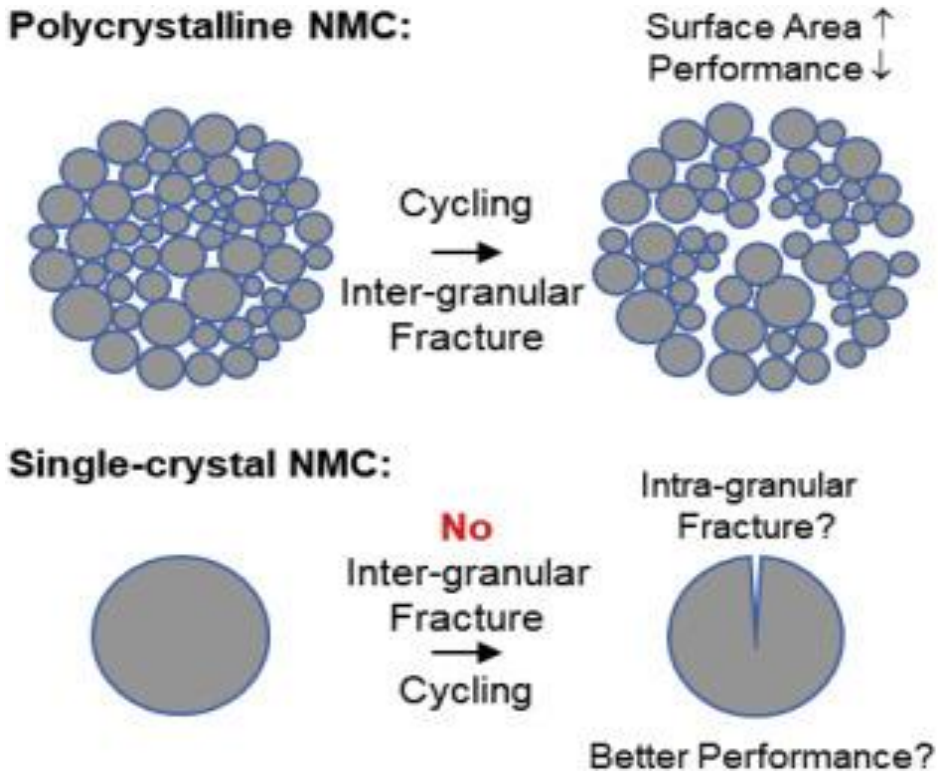
CEI/SEI film-formation additives and deep understanding of composition and structure of CEI/SEI

Surface Coating



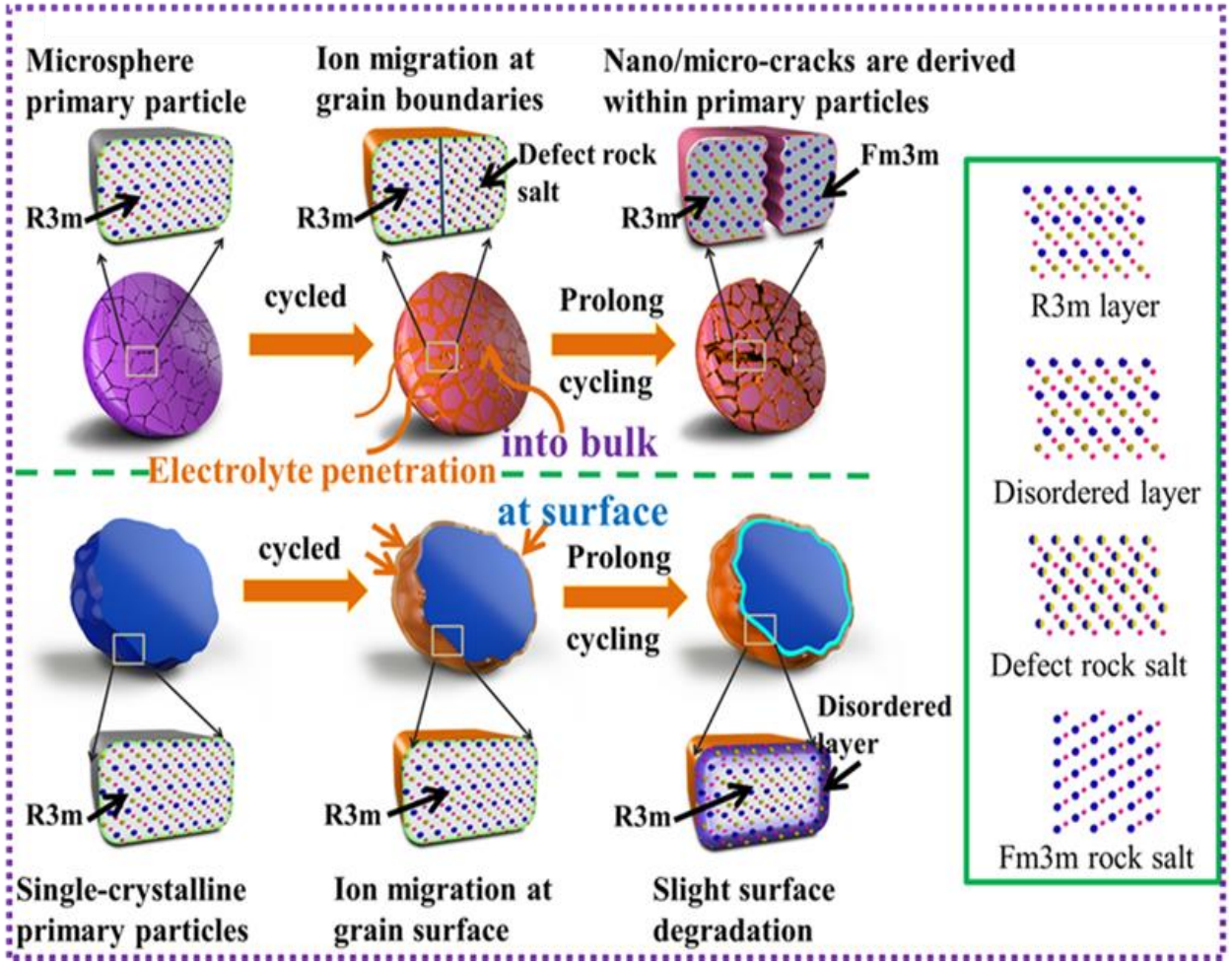
- **Precise Deposition Control of Surface coating with flexible and Ionic Conductively Surface layer**
- **ALD/MLD Coating**

NCM: polycrystalline vs single-crystalline



Absence of grain boundaries
High mechanical strength

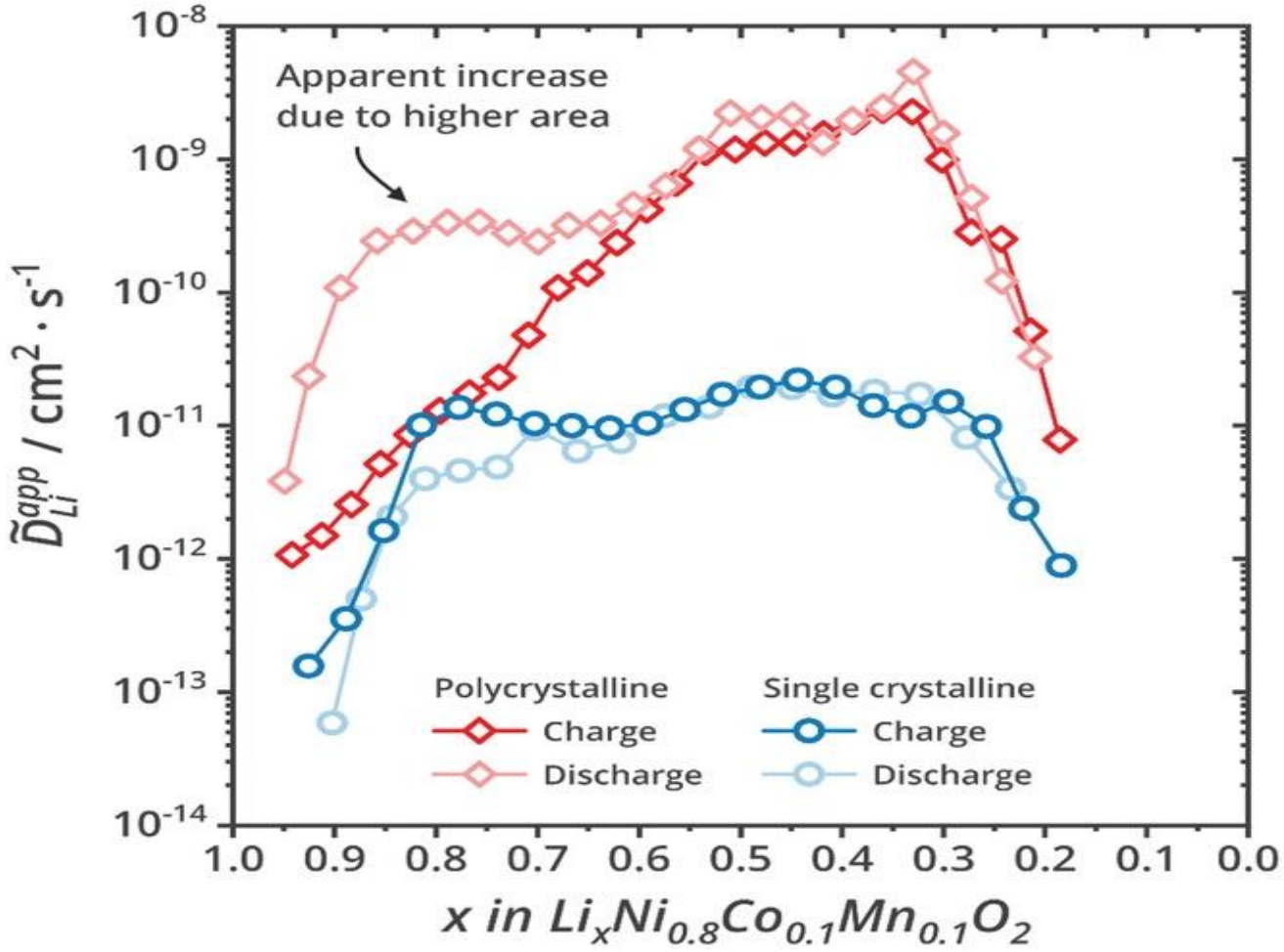
The degradation mechanism Ni-rich NCM: PC *vs* SC



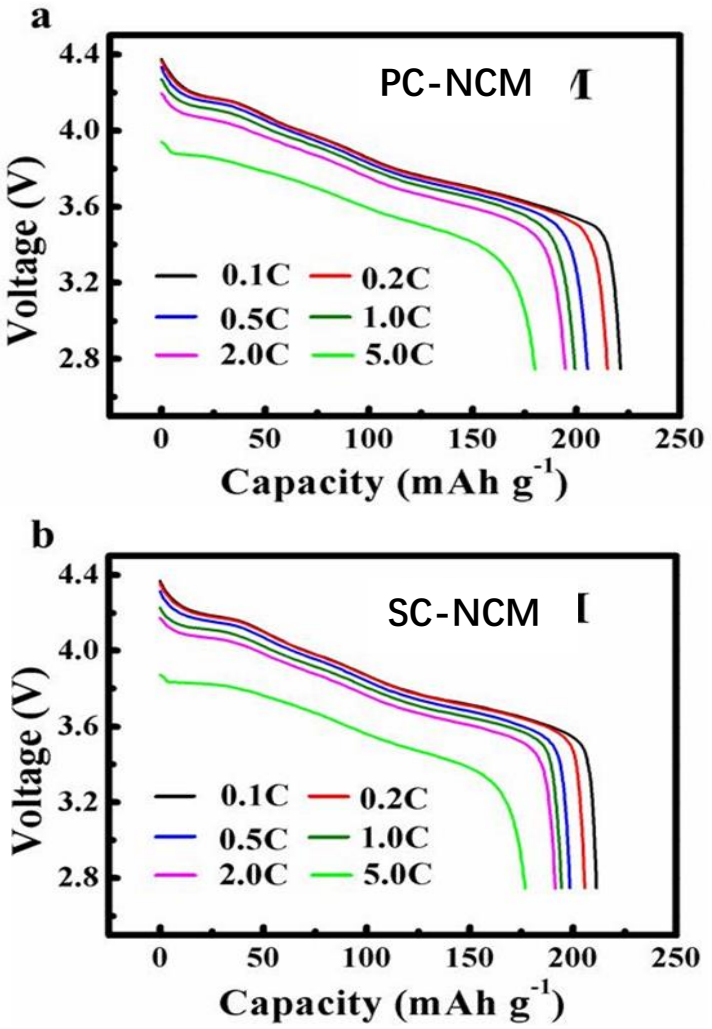
L. S. Lin, *Energy Storage Materials* **2020**, 27, 140;
J. P. Cho, *Adv. Mater.* **2020**, *32*, 2003040

X Fan, W Zhao, X Ou*, Y Yang*, Nano Energy,* **2020**, 70, 104450

The challenge of single-crystal NCM: intrinsic slower Li^+ transfer



Apparent lithium diffusion coefficient at 1st cycle

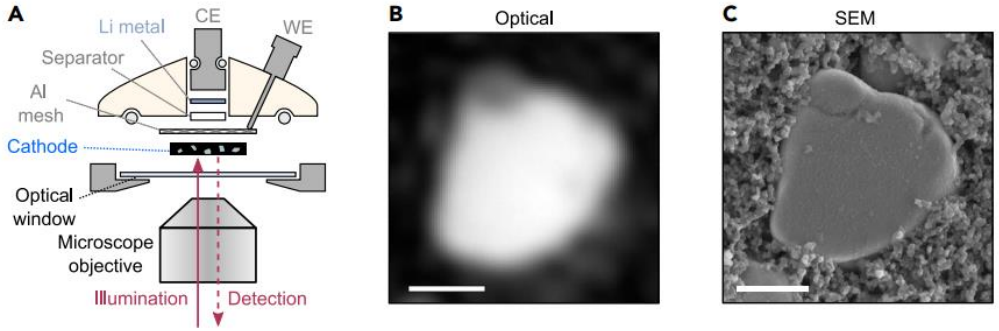


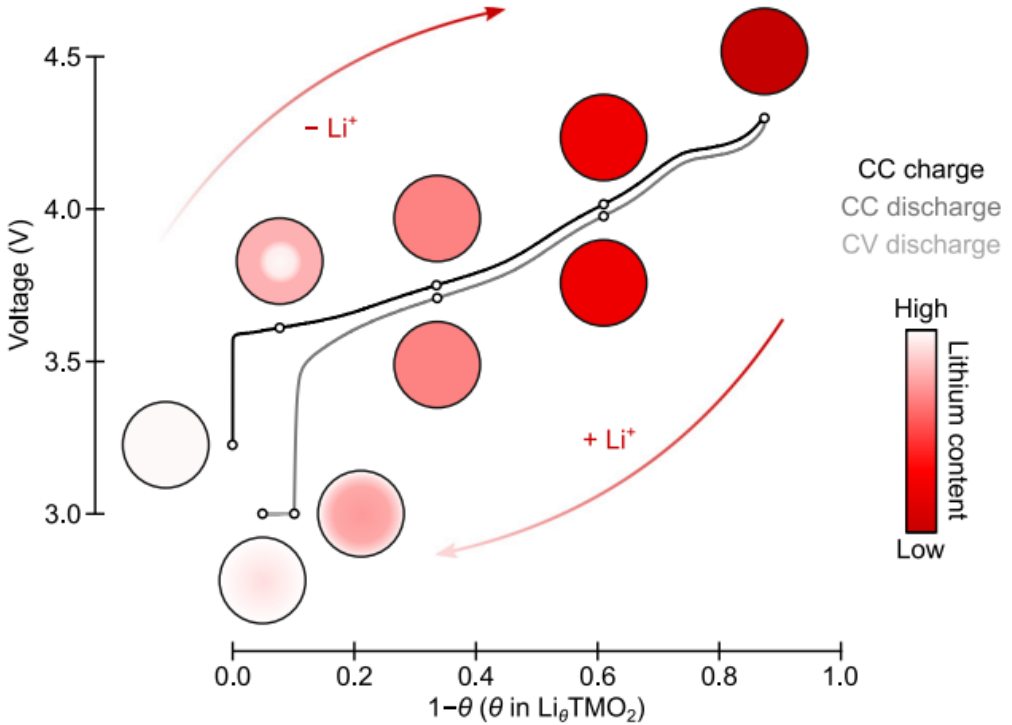
- **Rate cycling capability is unexpected due to intrinsic slower Li^+ transfer**

J. Janek, *Adv. Energy Mater.* **2021**, *11*, 2003400; *X Fan, W Zhao*, X Ou*, Y Yang*, Nano Energy*, **2020**, 70, 104450

Non-uniform reaction of SC NMC Cathode during C/Discharge processes

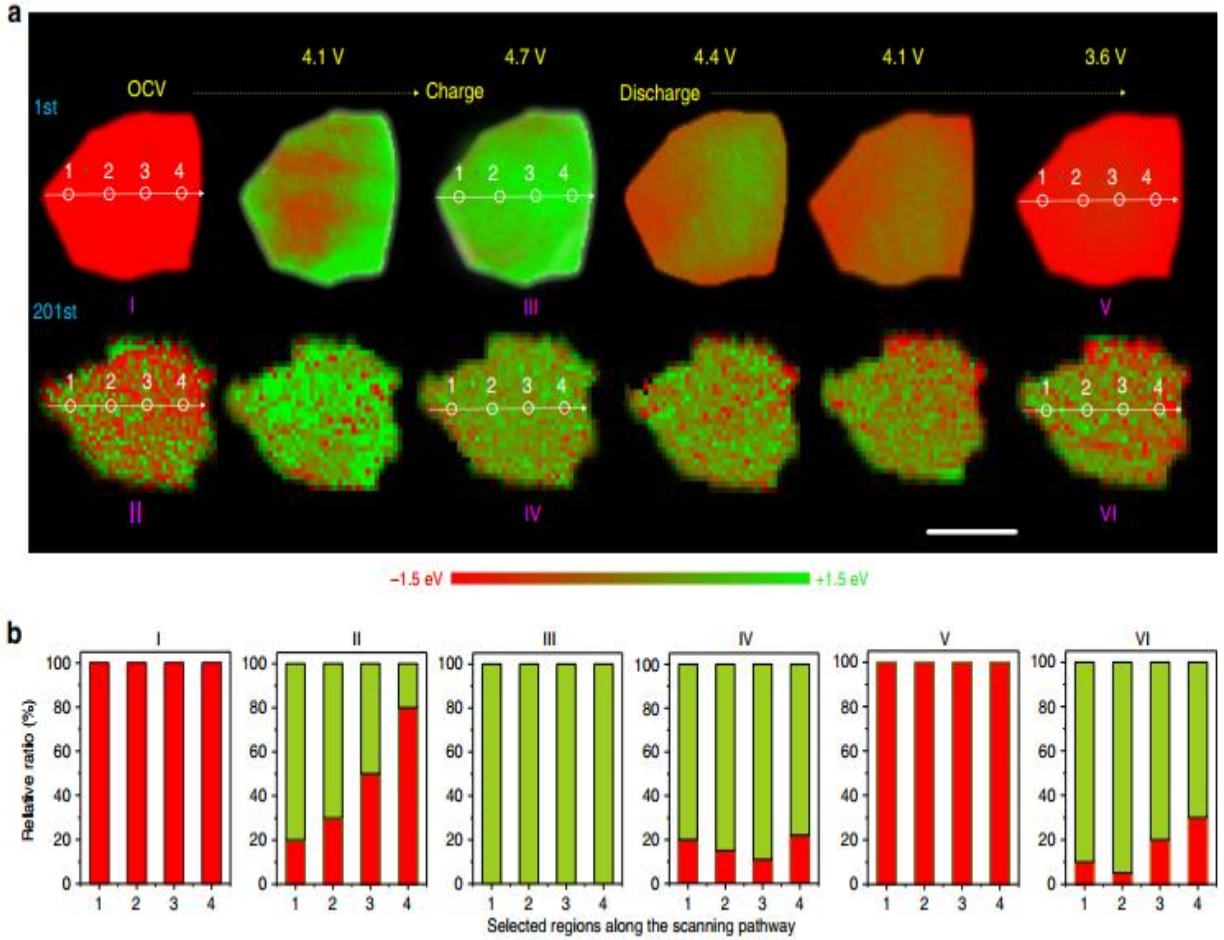
Operando optical microscopy of Single-crystal $LiNi_{0.87}Mn_{0.05}Co_{0.08}O_2$





C. P. Grey et al. Joule 2022, 6, 2535–2546

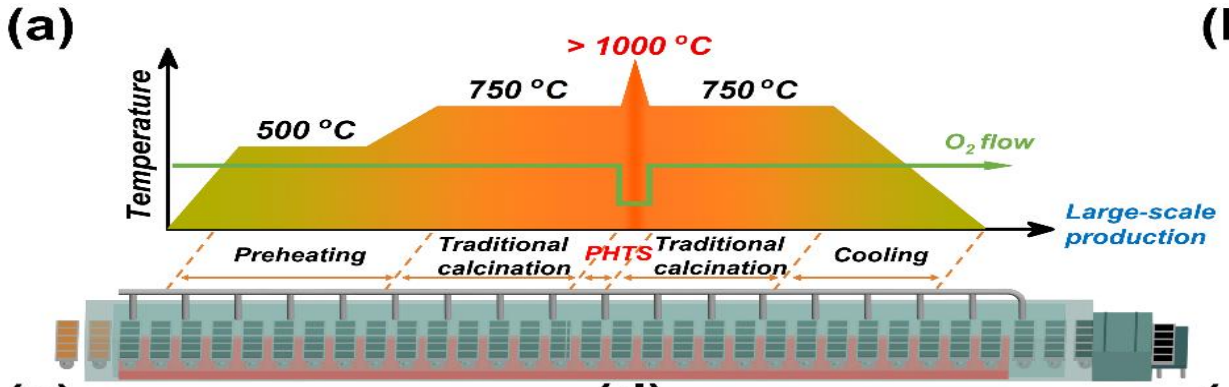
Ni k-edge 2D TXM-XANES of single-crystal NCM622

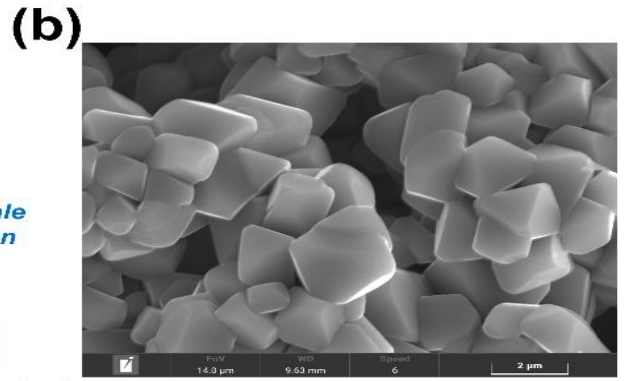


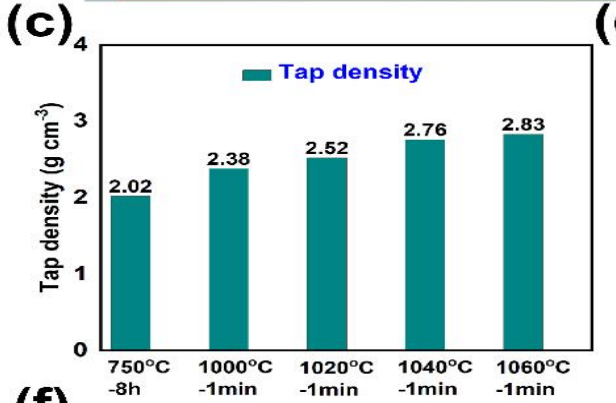
J. Lu eat al. Nature Communications, 2020, 11, 3050

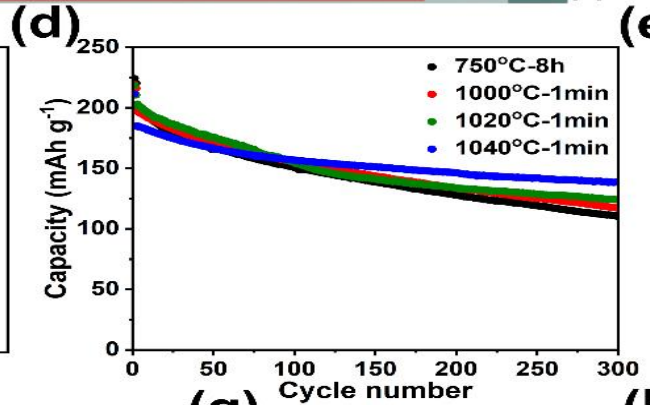
- **Non-uniform reaction results in Non-unifom Li disstribution。**

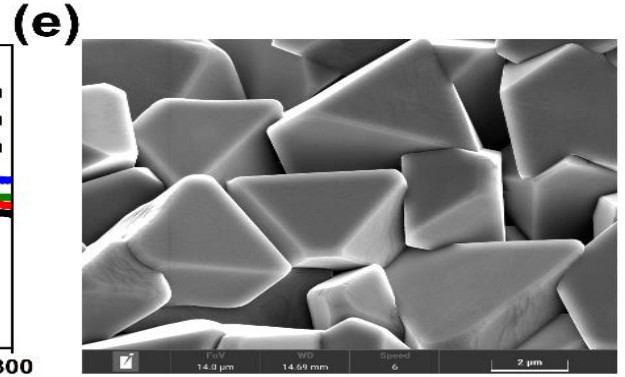
Synthesis of SC NMC with PHTS

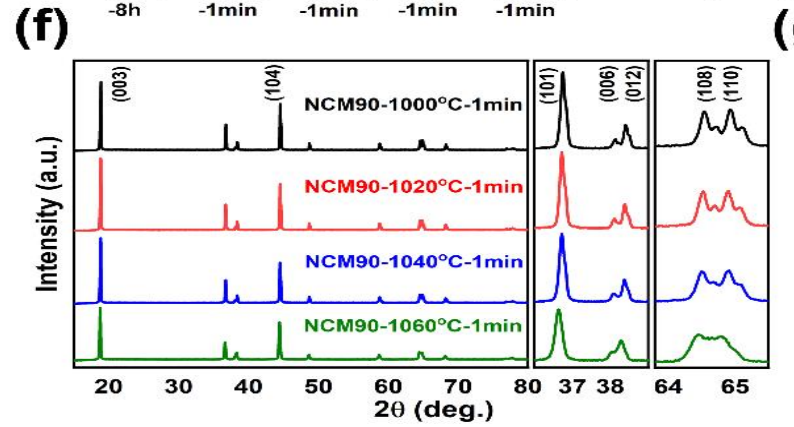


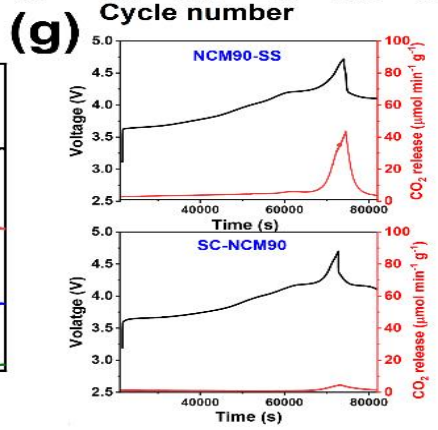


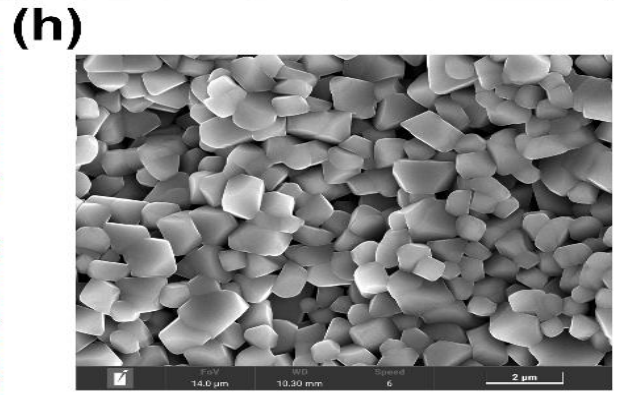








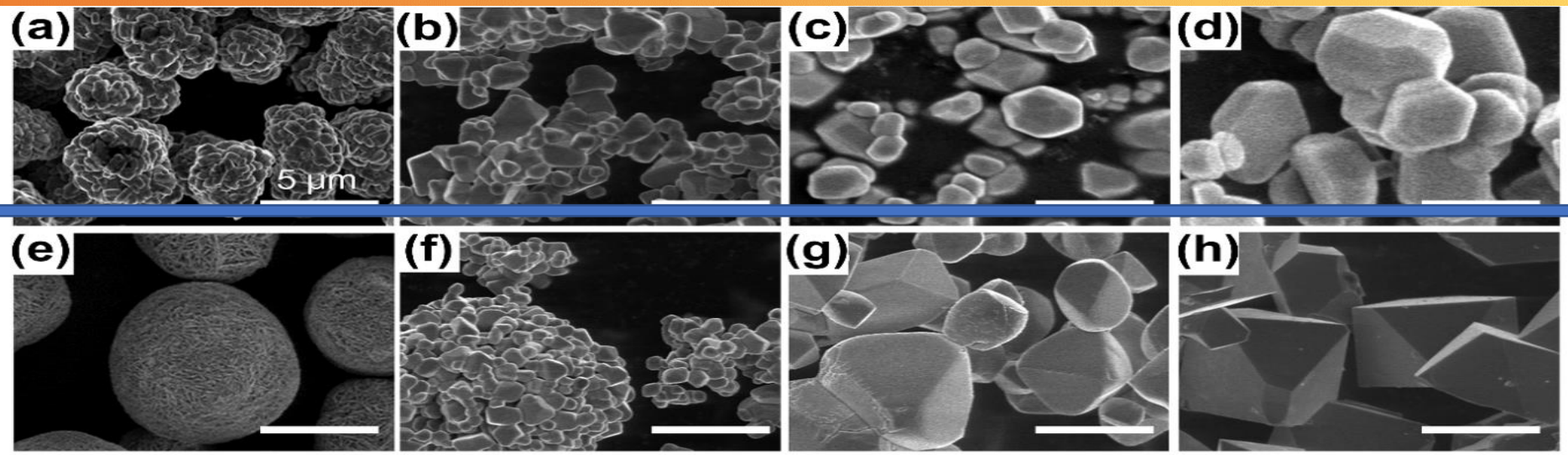




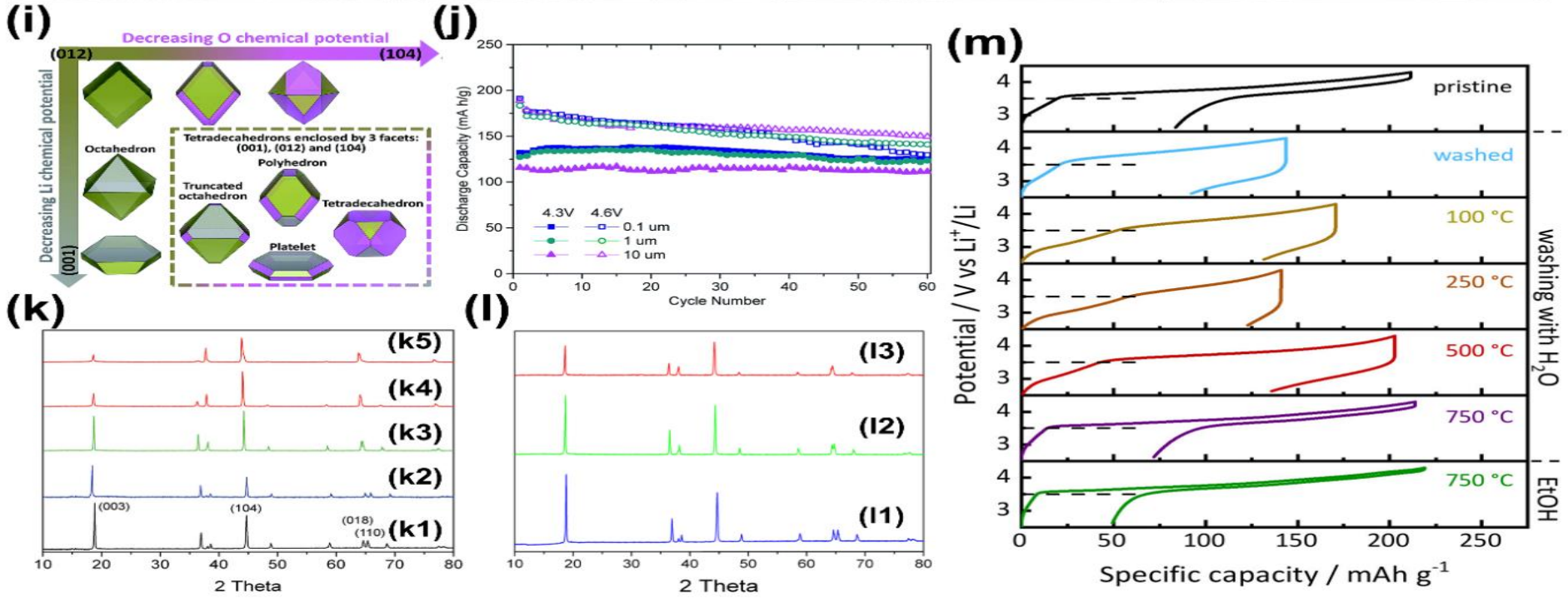
Ultrafast high-temperature sintering (UHTS) strategy

W. D. Zhou, et al; AEM, 2023

The Synthesis of Single Crystalline NMC, evolution of morphology and structure, and Electrochemical Performance after washing and secondary calciation



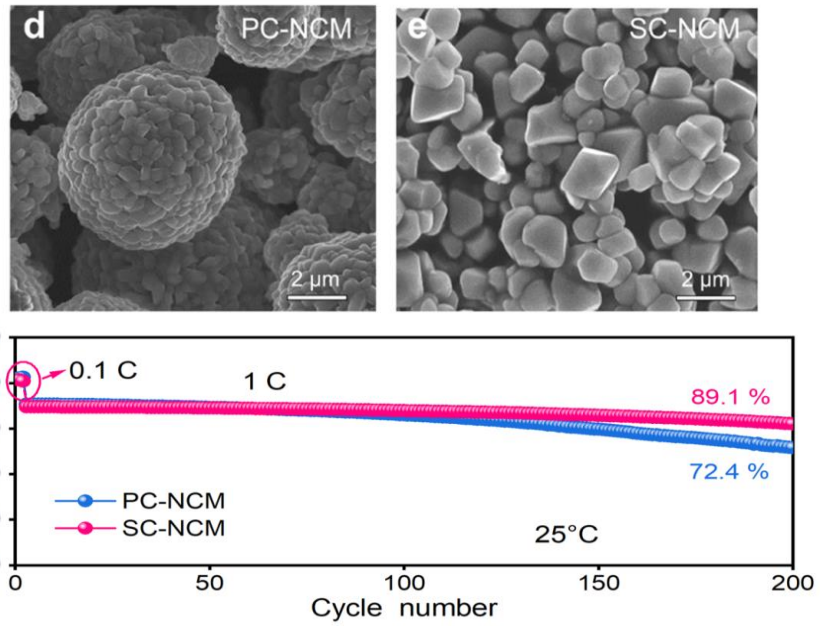
Temperature Increase

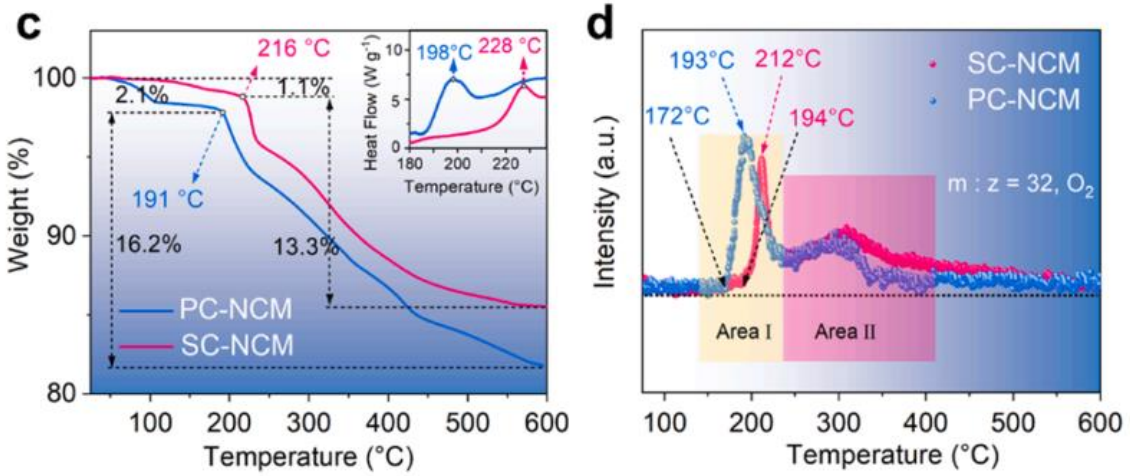


W. D. Zhou, et al; AEM, 2023

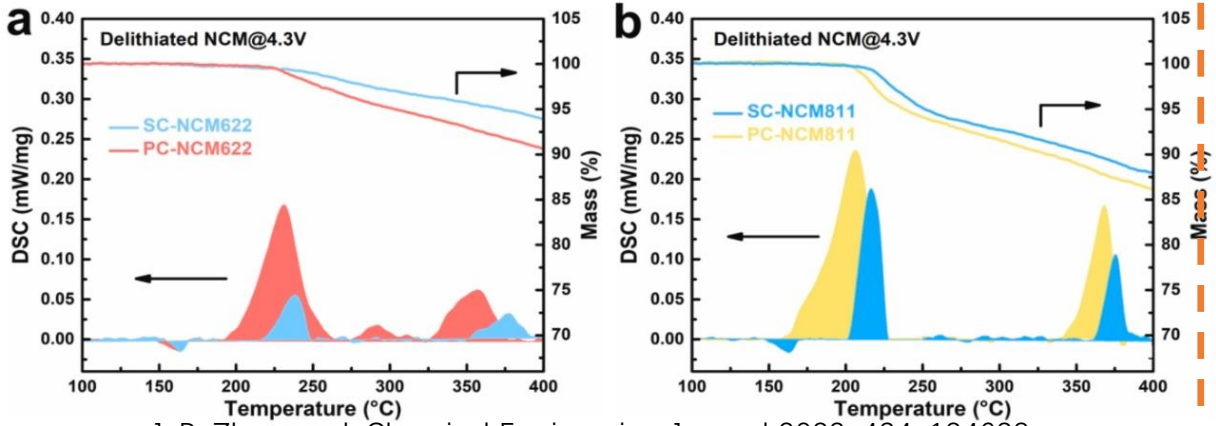
A comparison of SC & PC Ni-rich cathode: EC & Thermal

$LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$

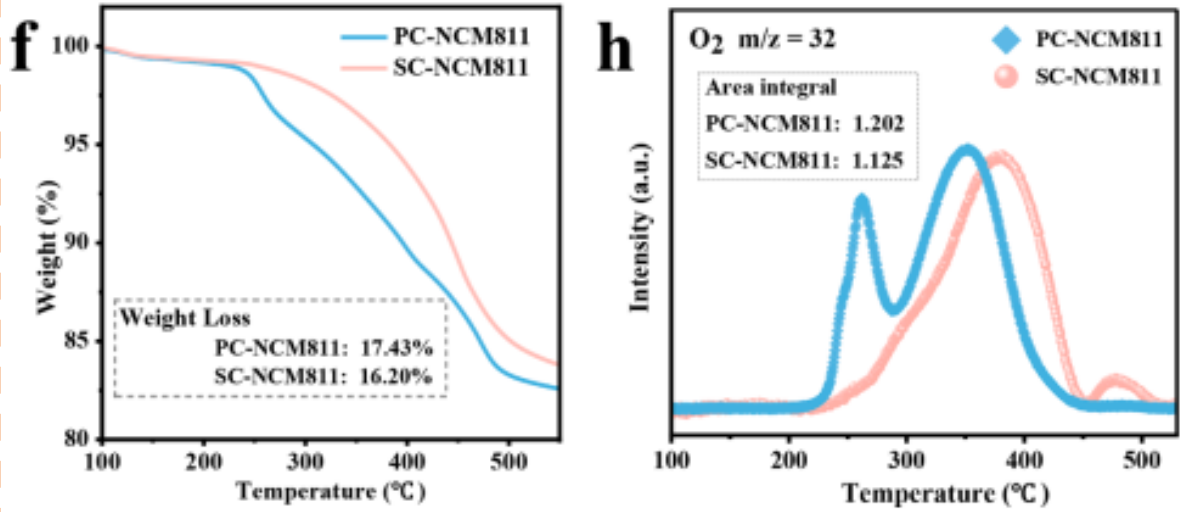




Q. Z. Xue et al. Nano Energy 2023, 116, 108846



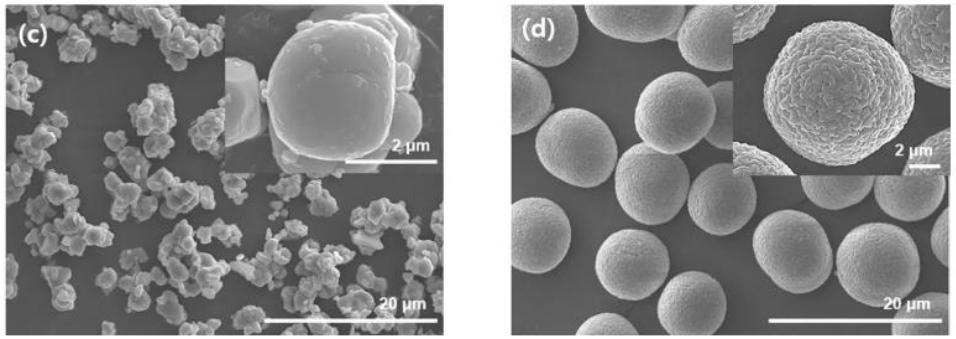
J. B. Zhao et al. Chemical Engineering Journal 2022, 434, 134638

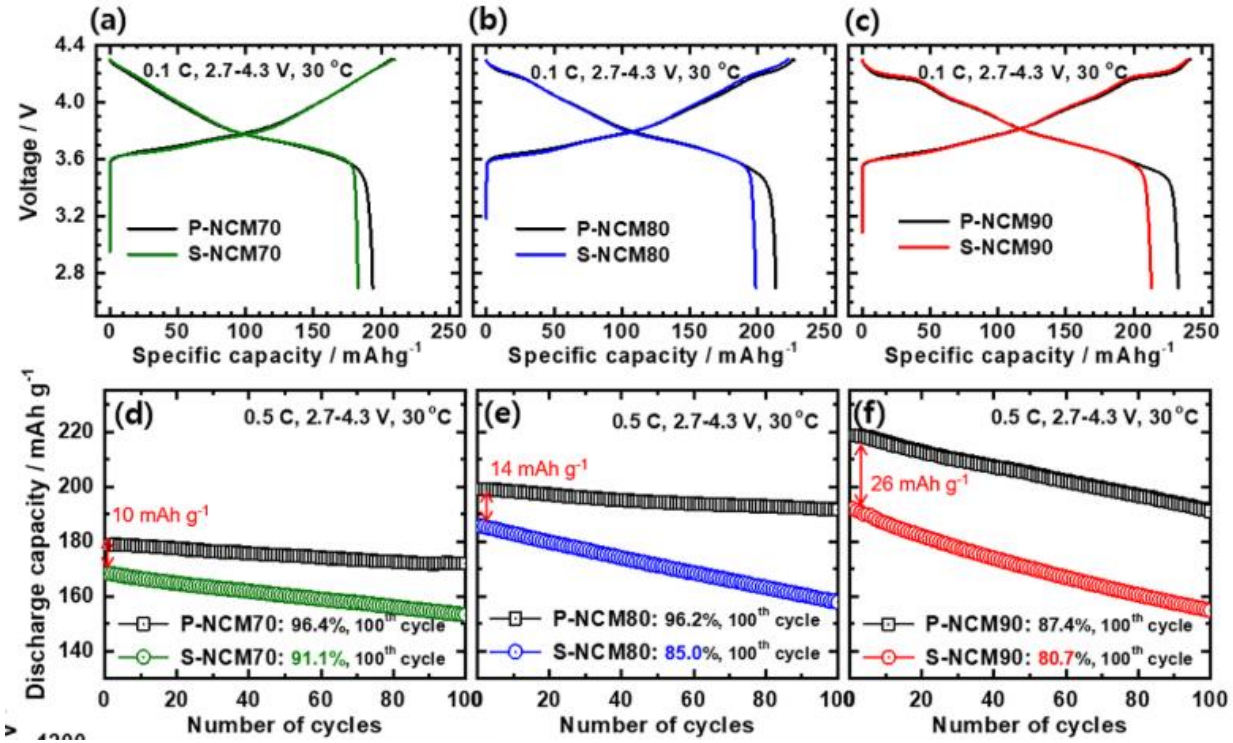


Q.S Wang et al. Energy Storage Materials 2023, 56, 495–505

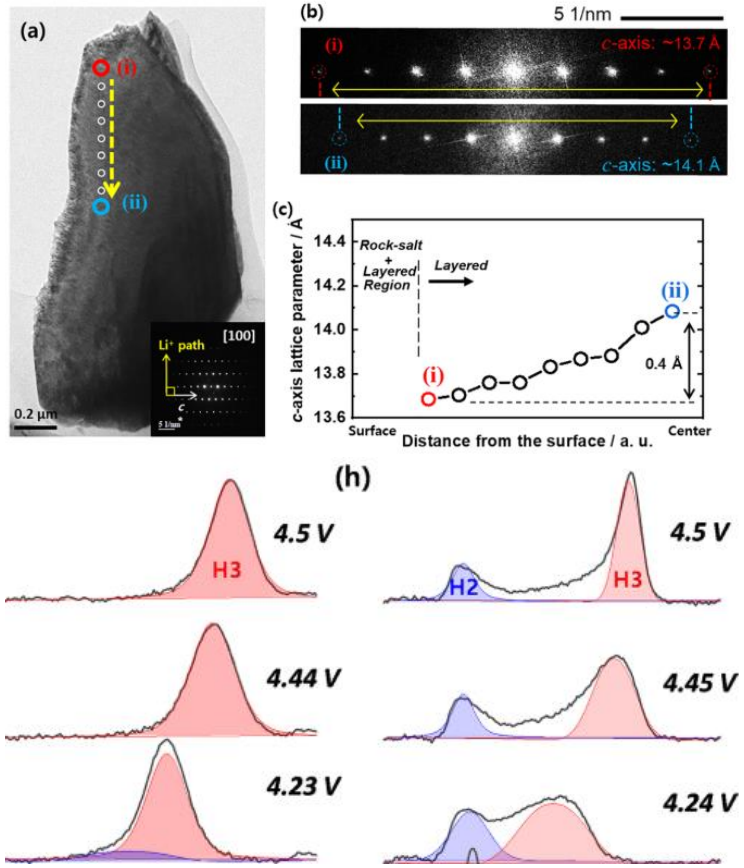
- **SC : Better EC & Thermal Stability**
- **It is necessary to consider the effects of Electrolytes, carbon and counter electrodes**

Degradation of SC Ni-rich Cathode & two-phase Separation





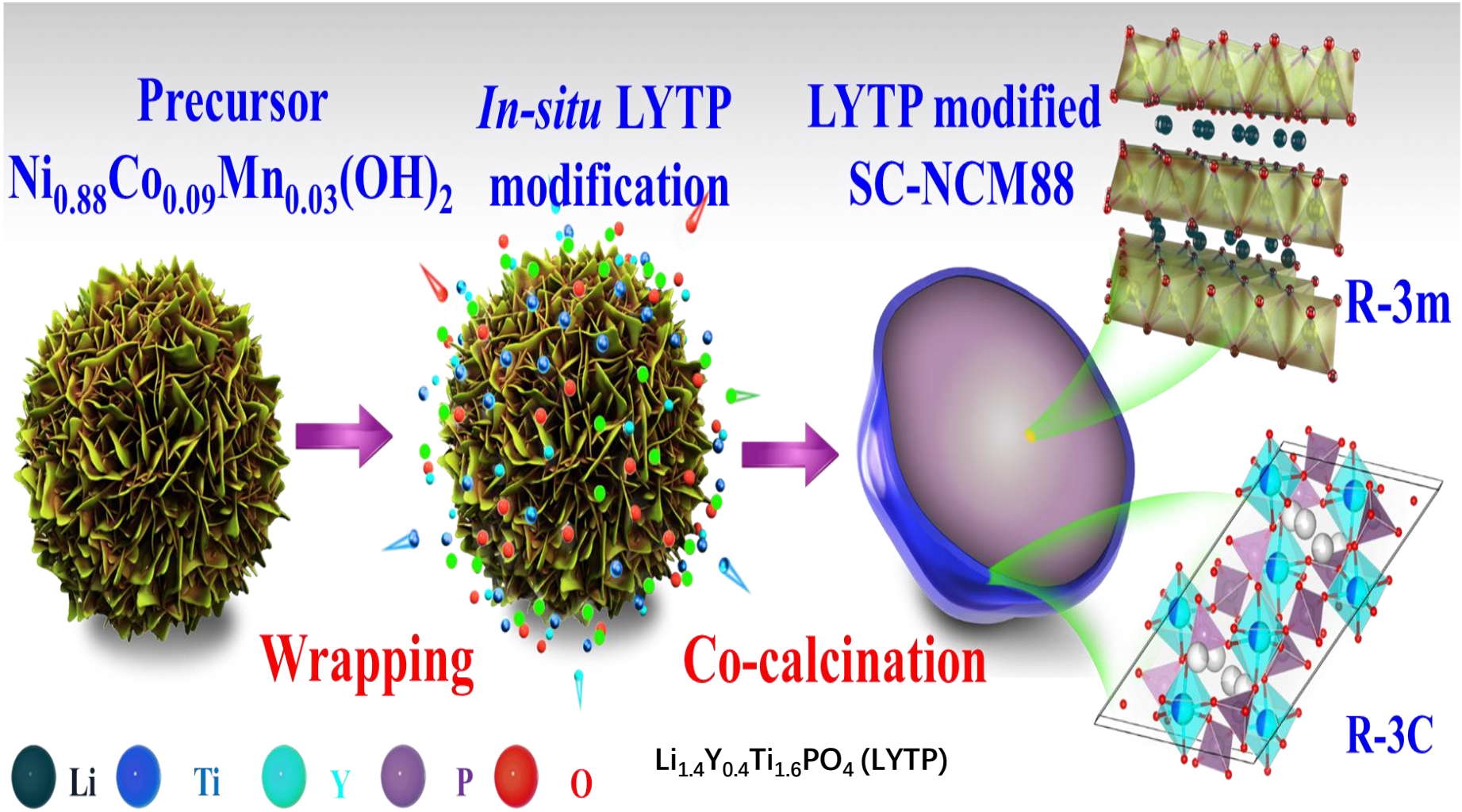
Y. K. Sun et al. ACS Energy Lett. 2021, 6, 2726−2734



- As Ni increase, more serious two-phase separation

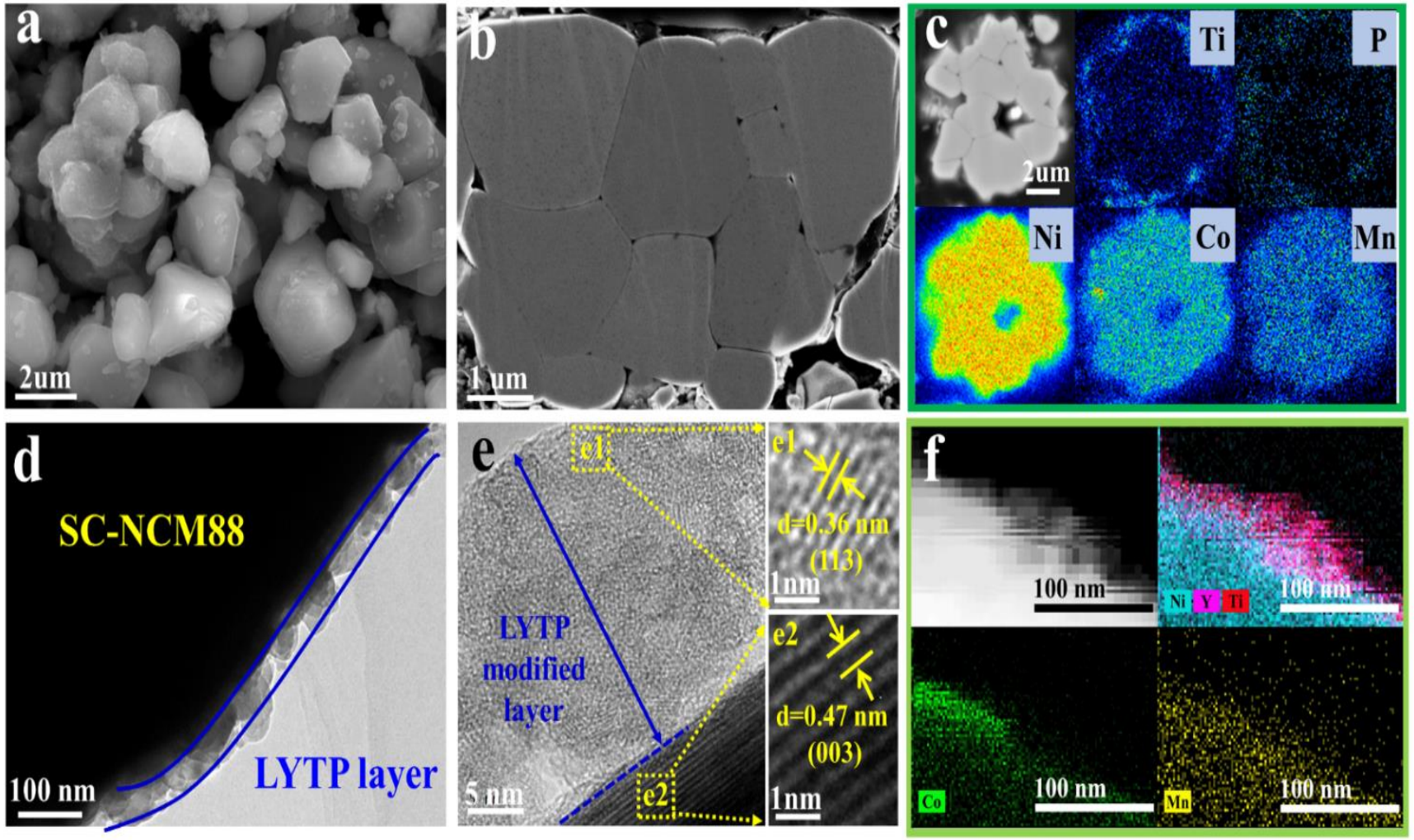
Serious non-uniformality due to low Li+ diffusion process and larger dedgradation。

In situ inorganic conductive network formation in high-voltage single-crystal Ni-rich NCM cathodes



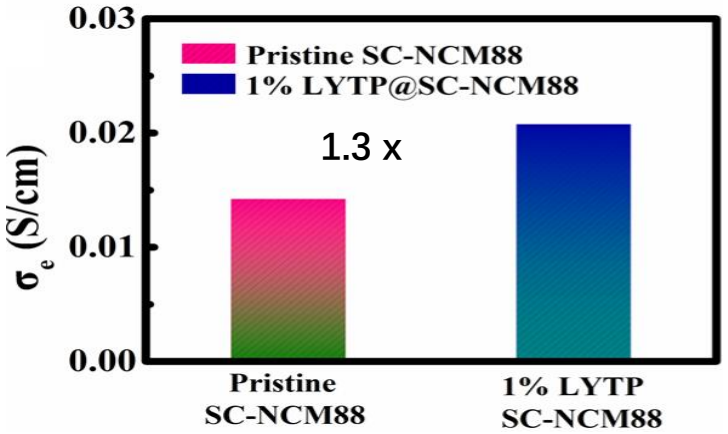
X Fan, W Zhao*, X Ou*, C Battaglia, Y Yang*, Nature Communications, **2021**, 12, 5320

Conformal coating on the surface of SC-NCM88

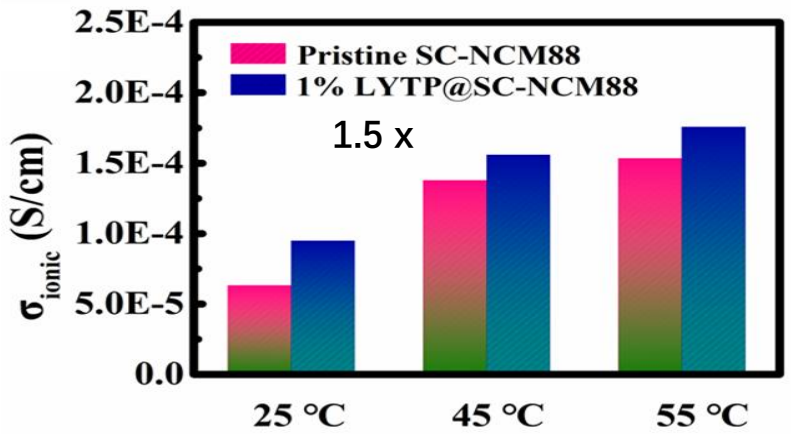


- In-situ coating strategy builds a conformal and uniform coating on the surface of SC-NCM88 particles

Enhanced conductivity of LYTP@SC-NCM88

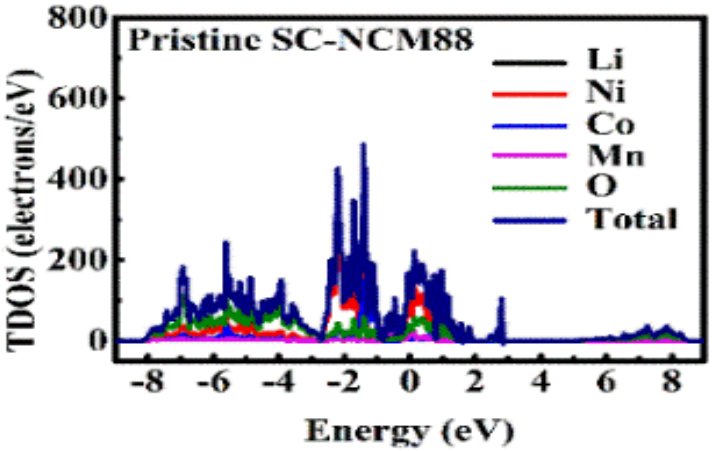


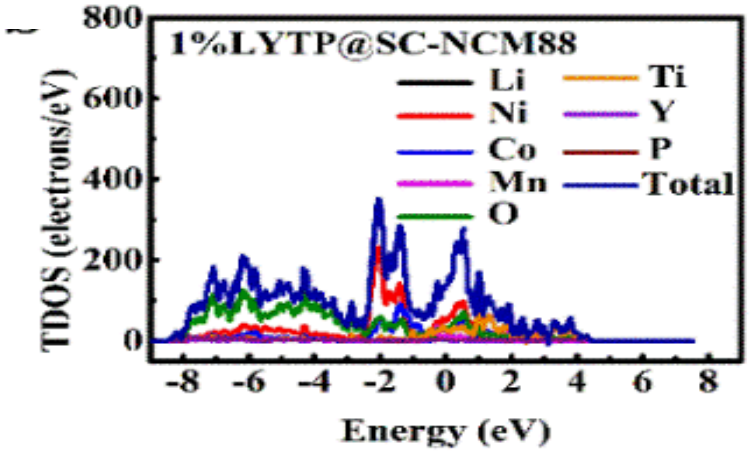
Li^+ conductivity



Electron conductivity

Higher TDOS after coating

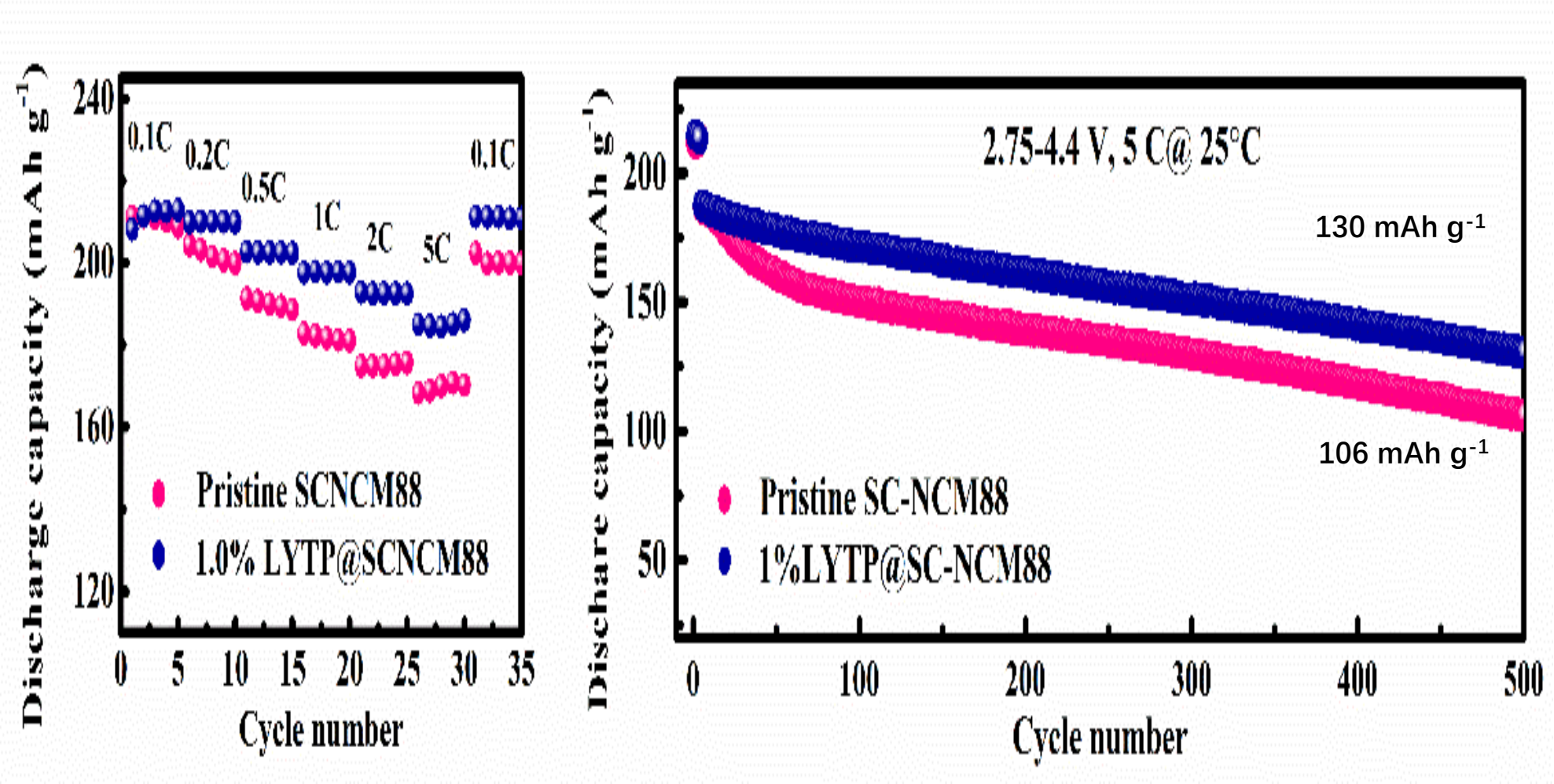




Total electron density of states

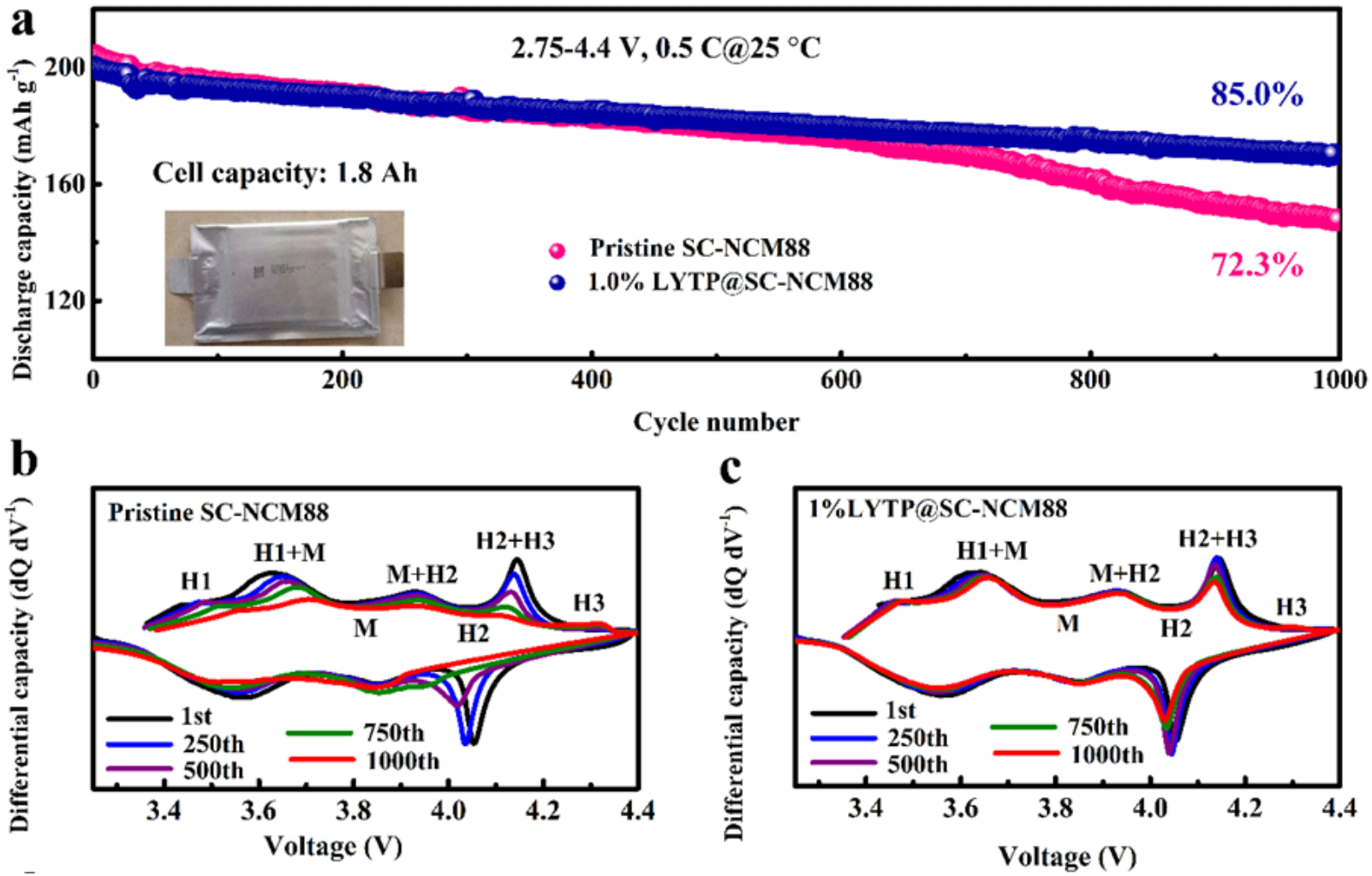
- **Li conductivity and electron conductivity both improved after coating**

Enhanced cycling capability at high specific current



- LYTP@SC-NCM88 delivers better rate performance and superior cycling at high specific current as the benign Li^+ transport network between particles due to integrated LYTP network

Superior long-term cycling and enhanced H2-H3 reversibility

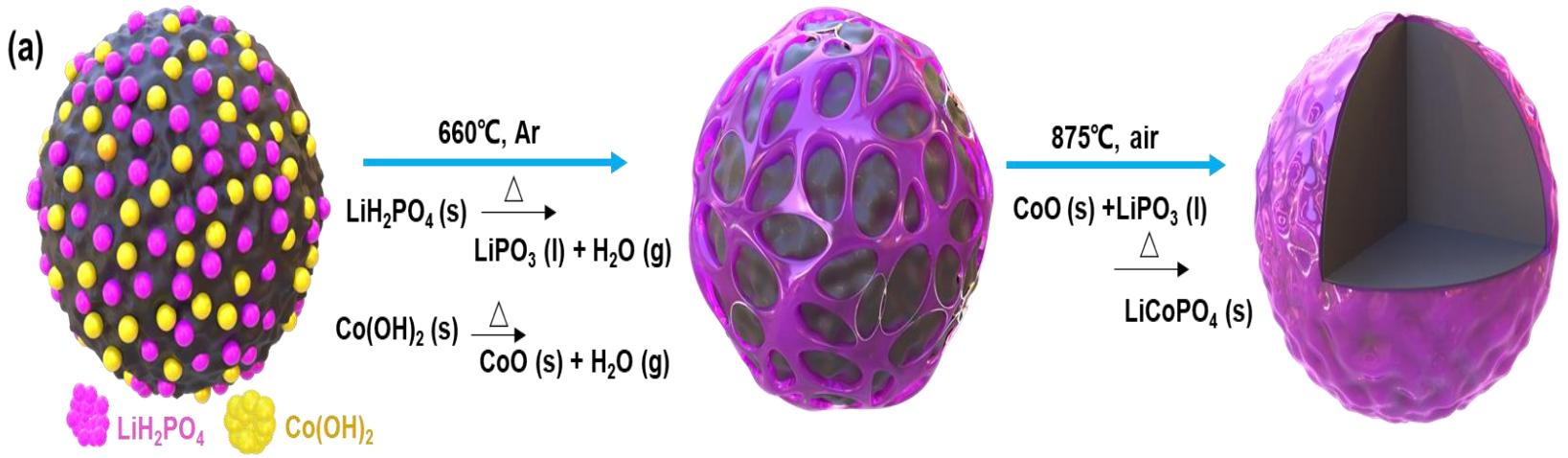


- LYTP@SC-NCM88 enhances the cycling capability and H2-H3 reversibility due to the effective protection on the surface of SC-NCM88 and benign Li^+ transport network between particles

Pushing Lithium Cobalt Oxides to 4.7 V by Lattice-Matched Interfacial Engineering

X.R. Yang, Y. Yang*, et al; **Advanced Energy Materials;**
2022, 2200197

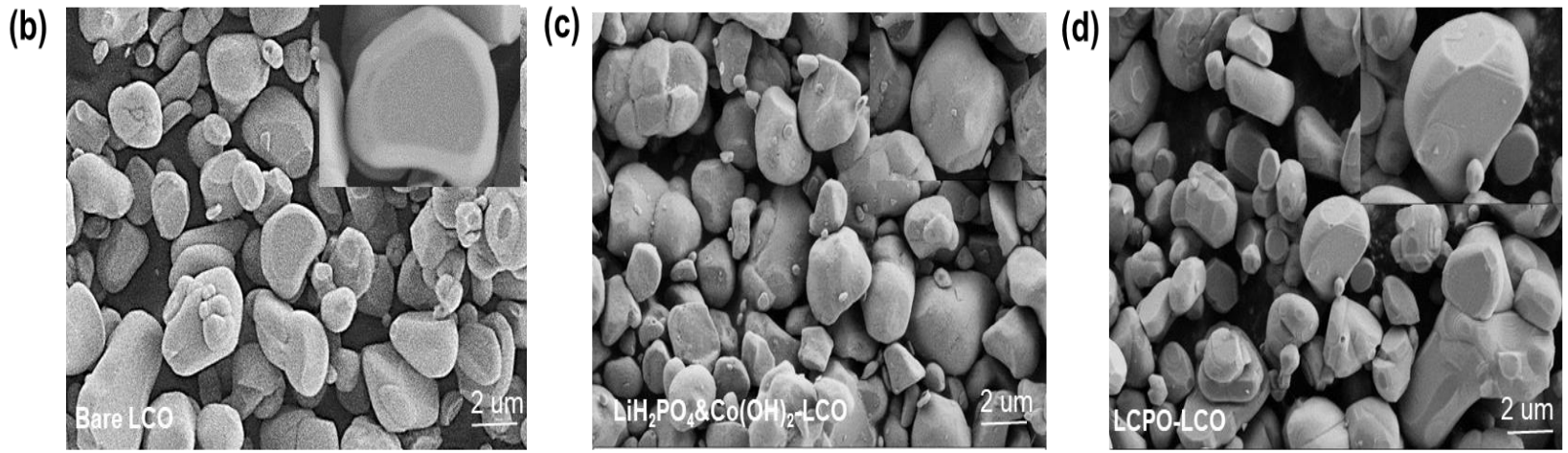
$LiCoPO_4$ (LCPO)-coated LCO (Calcination & SEM)



$$LiH_2PO_4(s) \rightarrow LiPO_3(l) + H_2O(g)$$

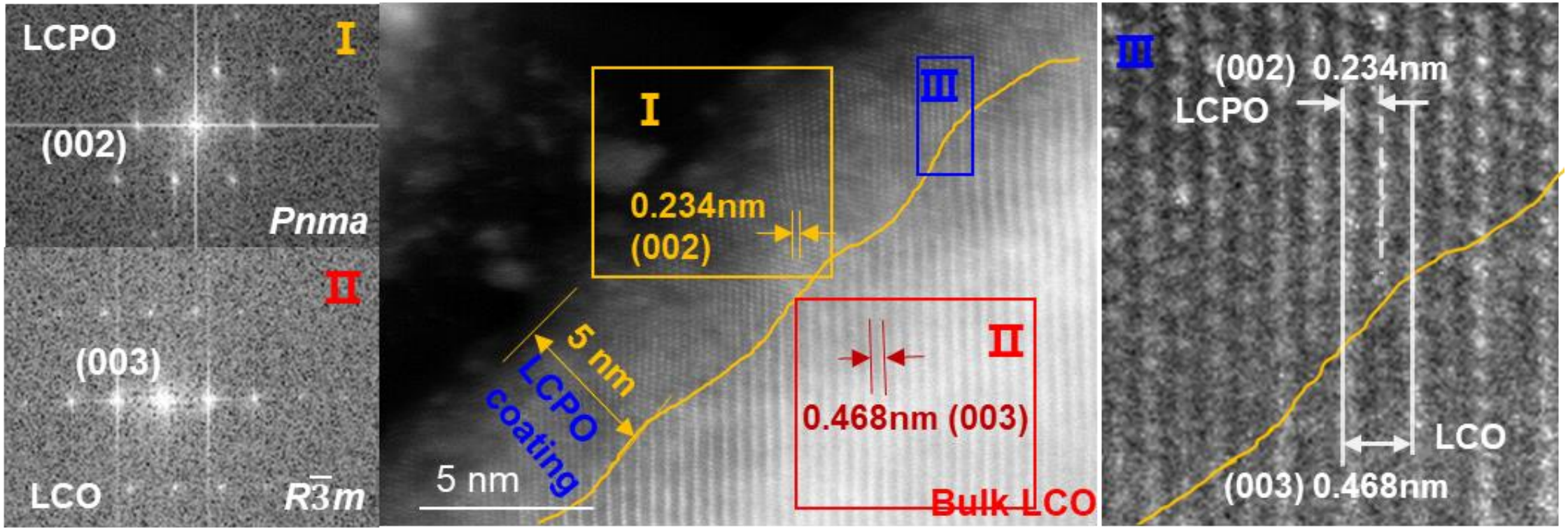
$$Co(OH)_2(s) \rightarrow CoO(s) + H_2O(g)$$

$$LiPO_3(l) + CoO(s) \rightarrow LiCoPO_4(s)$$



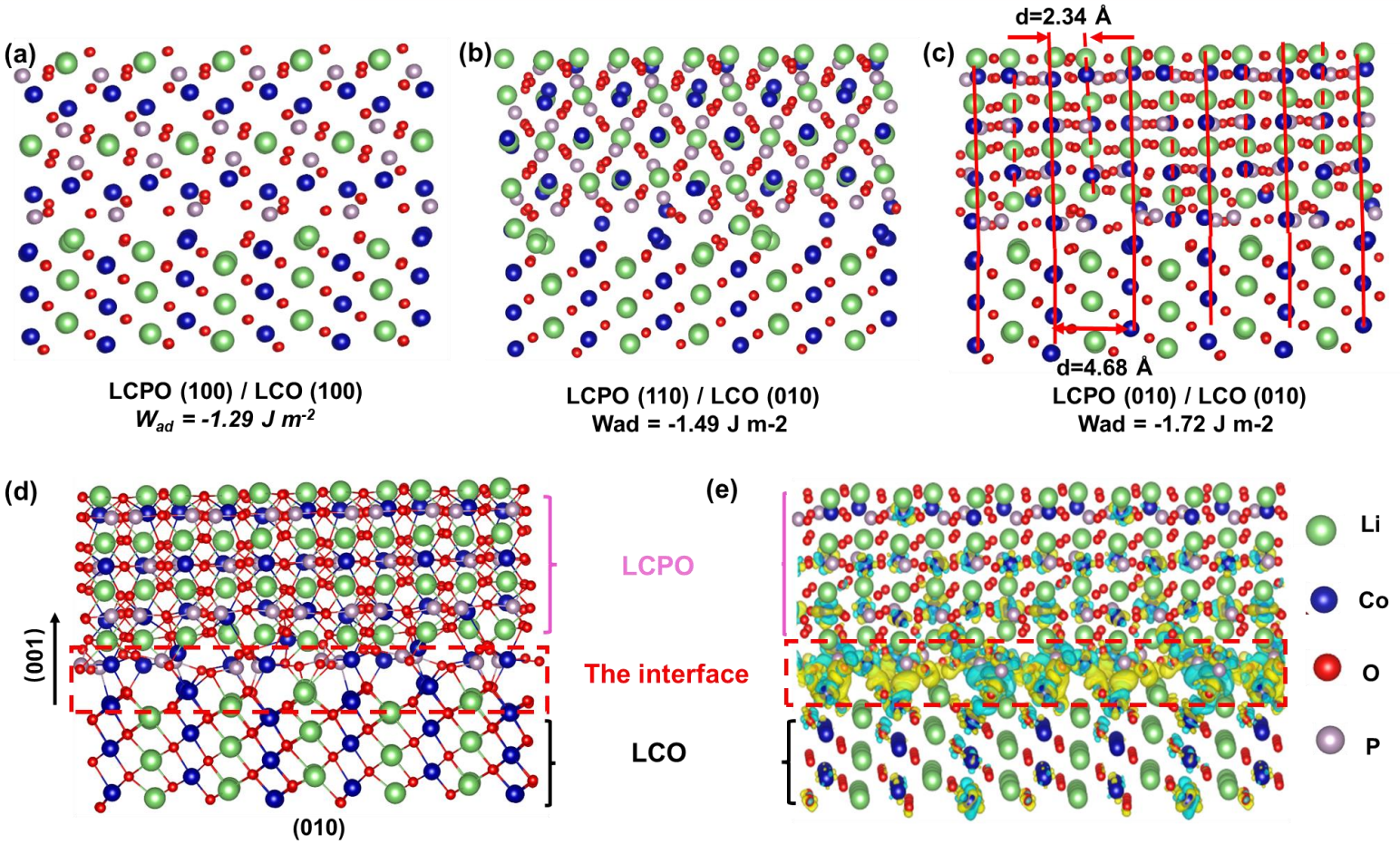
✓ At 660 ℃ Melted **$LiPO_3$ could be coated On LCO**, coated LCO is smooth as well as to the pristine LCO

HAADF-STEM Images of LCPO@LCO



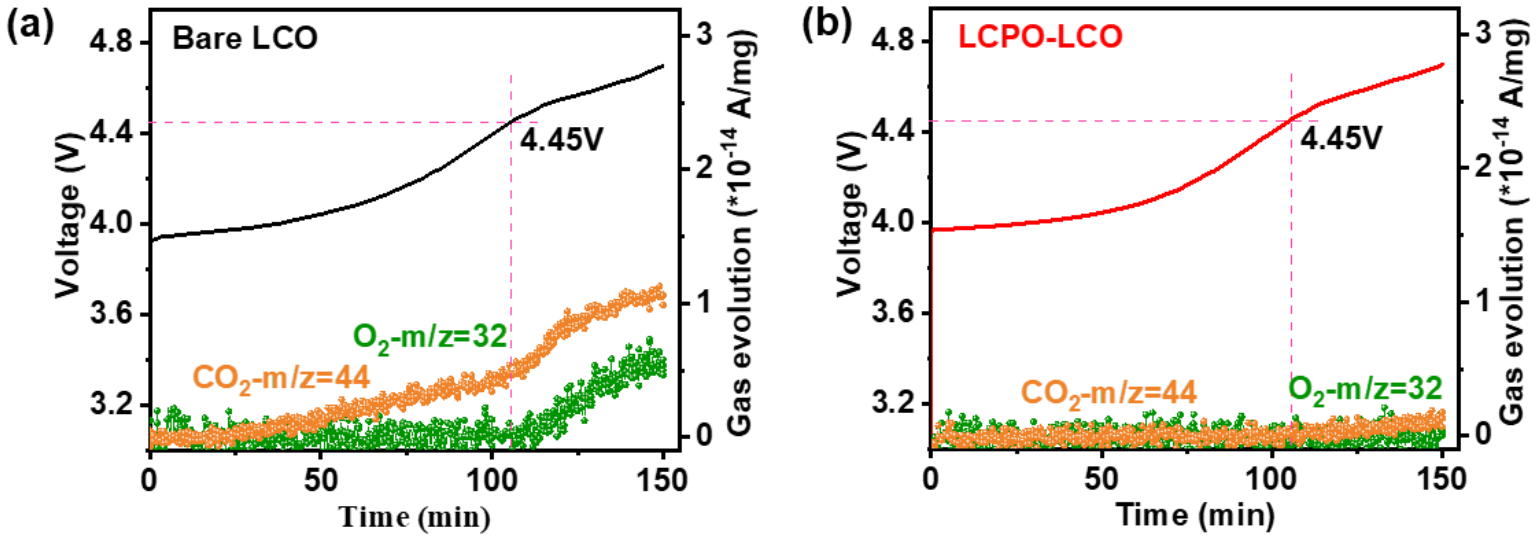
- ✓ （002）of LCPO grows along with (003) of LCO的（003），
  - ✓ Region Ⅲ could see such expital relationship at the interfaces

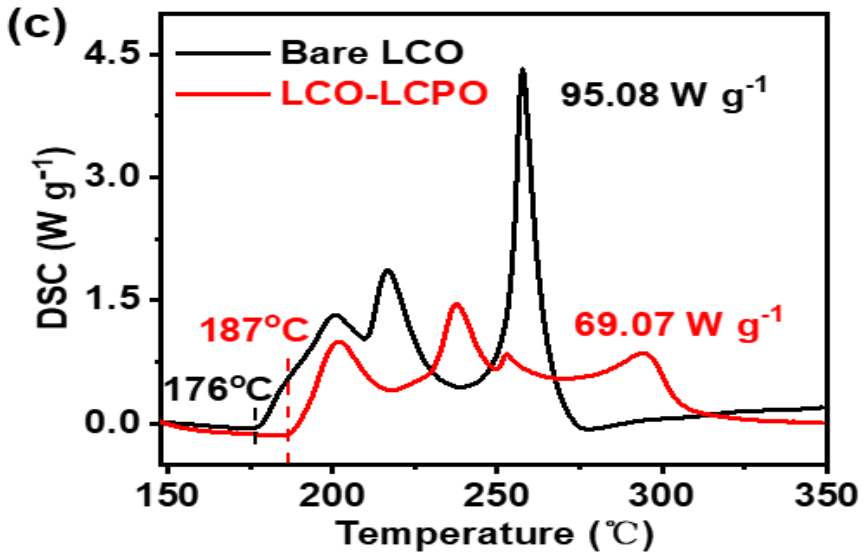
LCPO在界面处的外延生长模型



- ✓ LCO(010)与LCPO(010)界面间的**W_{ad}值最低**，说明二者之间的**相互作用更强**，有利于共晶格界面的形成
- ✓ LCPO(002)晶面间距**（2.34Å）**等于LCO(003)晶面间距**（4.68Å）**的一半
- ✓ **界面连接处**，LCO表面的O原子可以与LCPO中的P/Co原子**形成强的共价键**

LCPO包覆层对电解液分解和O释放的抑制

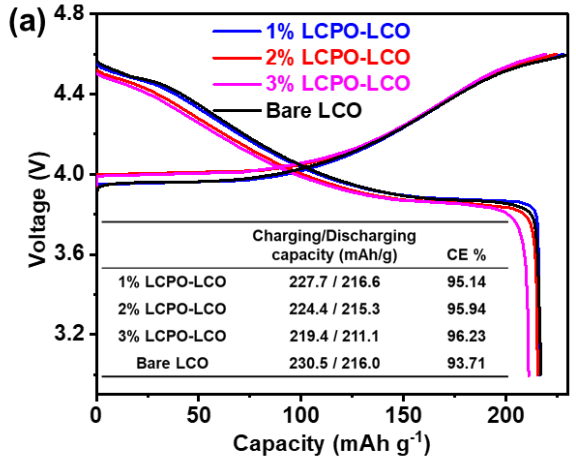


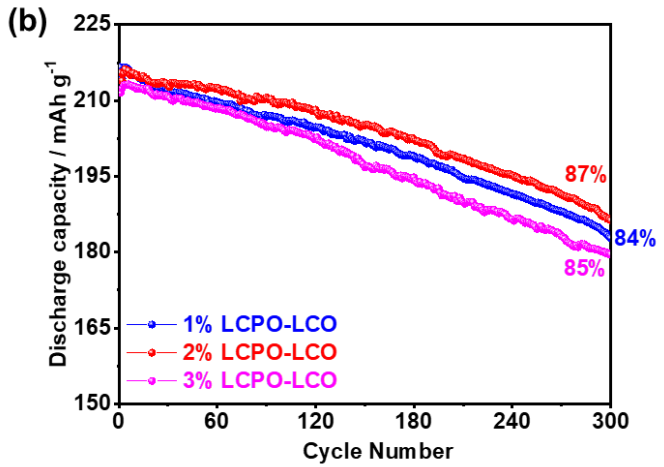


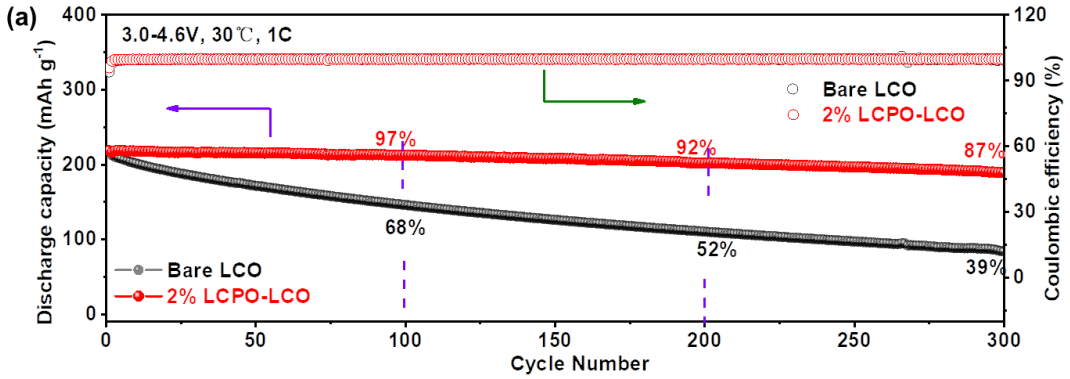
电解液：1 M LiPF6-EC/EMC(3:7)+ 5%FEC+ 1% SUN

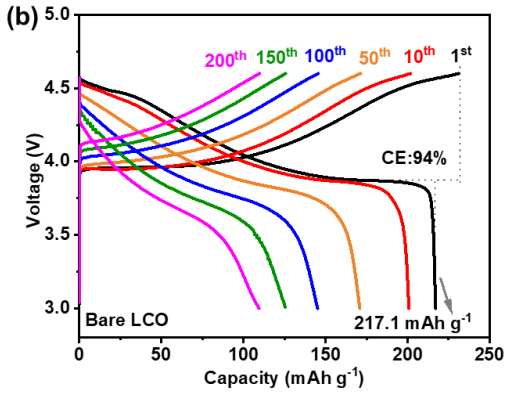
- ✓ 晶格O^{2-}氧化形成的O^{-}具有**高移动性**，容易从晶体结构中逸出
- ✓ 高活性的**O^{-}**会显著**加剧电解液氧化分解**
- ✓ O^{2-}的部分氧化降低了Co和O之间的共价键，形成**欠配位的O和O-O键**，在高温时**诱导O_2释放**，**降低电池安全性**，LCPO包覆有效的改善了LCO晶格氧的稳定性

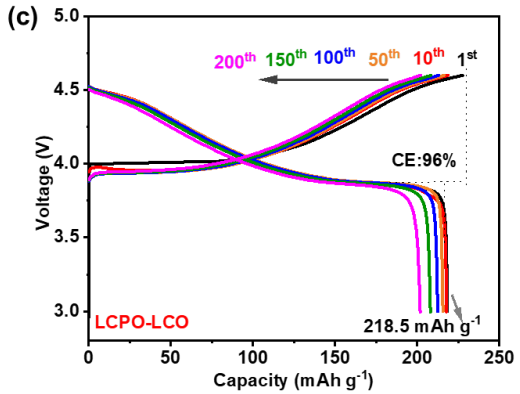
Electrochemical Performance of LCPO-LCO





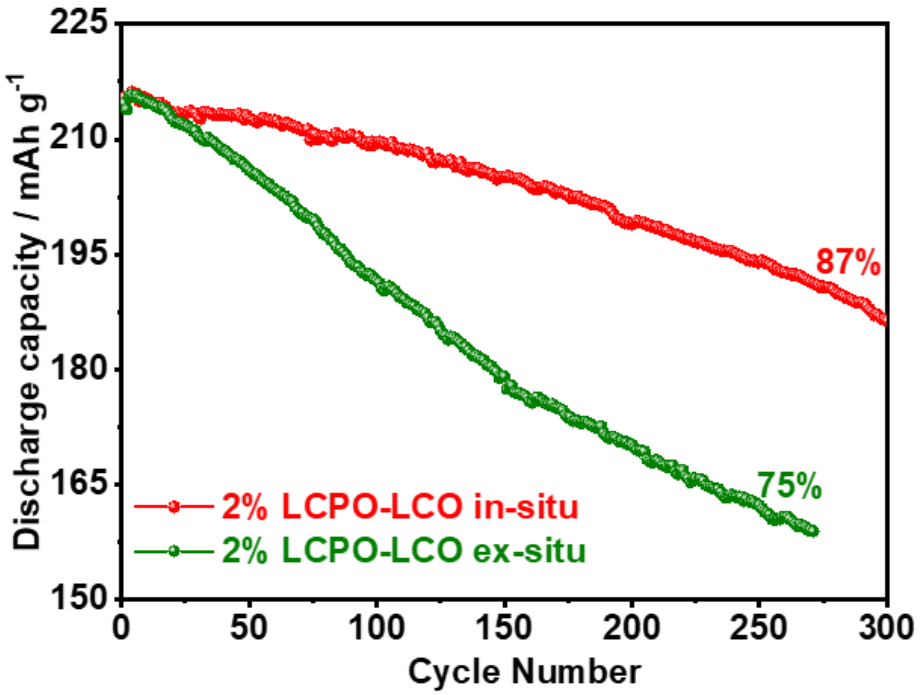


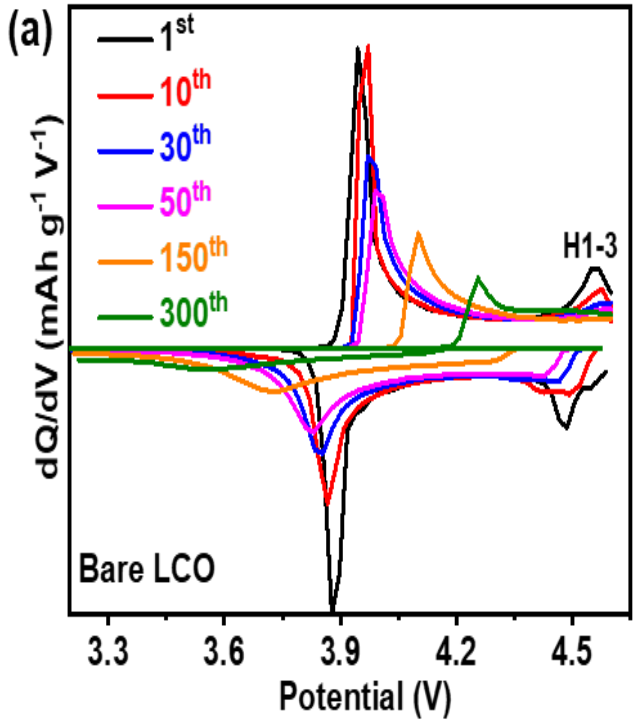


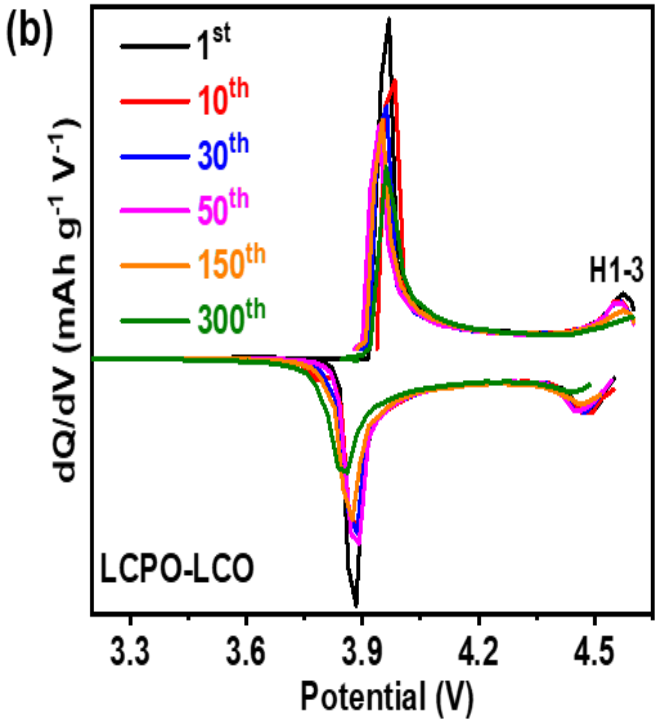


- ✓ **Higher Coulombic efficiency After LCPO coating, indicating a suppression of side reactions between LCPO-LCO and Electrolytes**
- ✓ **2% LCPO-LCO has higher capacity and capacity retention (87%)**

In-situ or Ex-situ Coating of LCPO-LCO

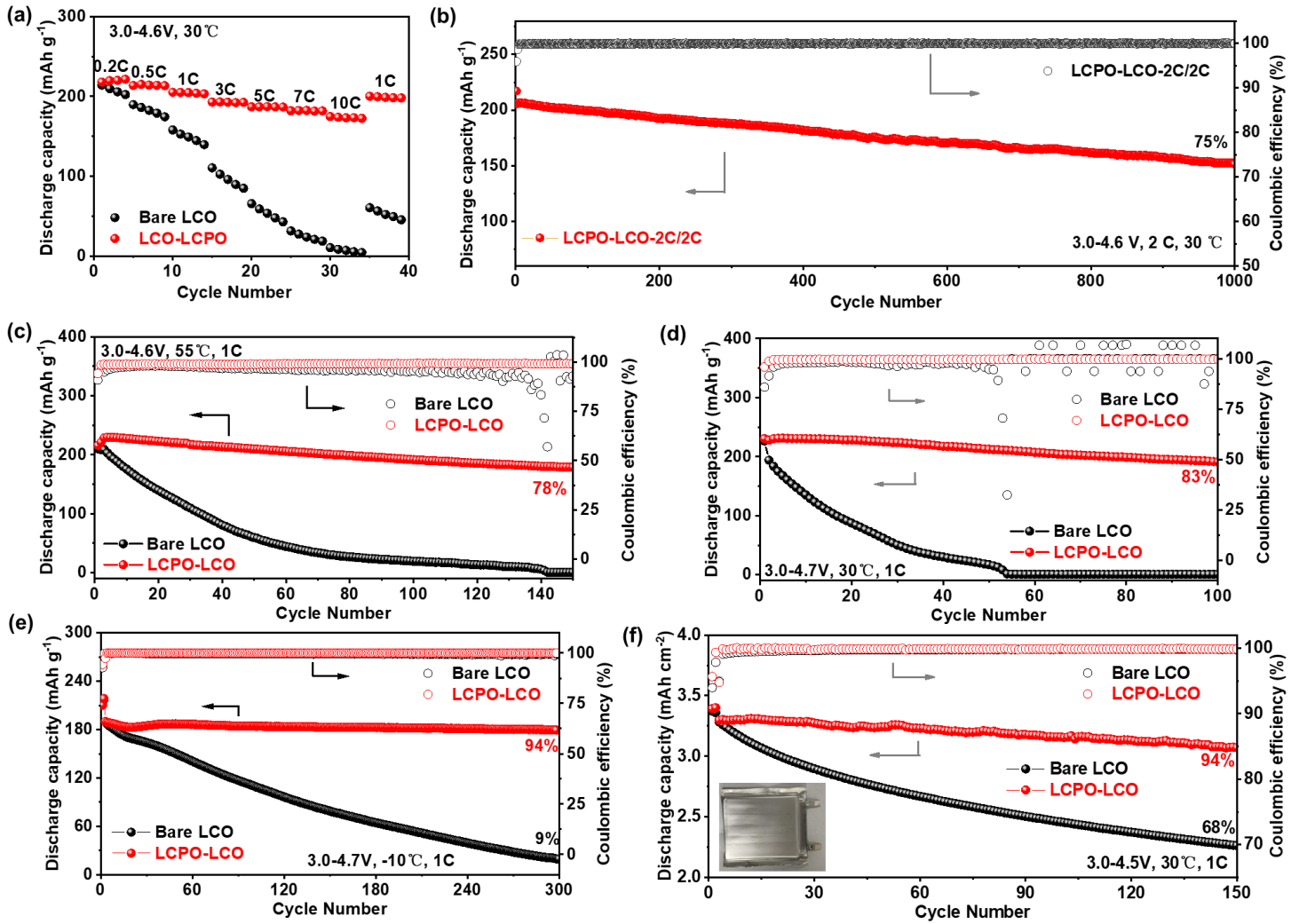






✓ **Much Better Performance of LCPO@LCO due to suppression fo irreversible conversion of H3 phase**

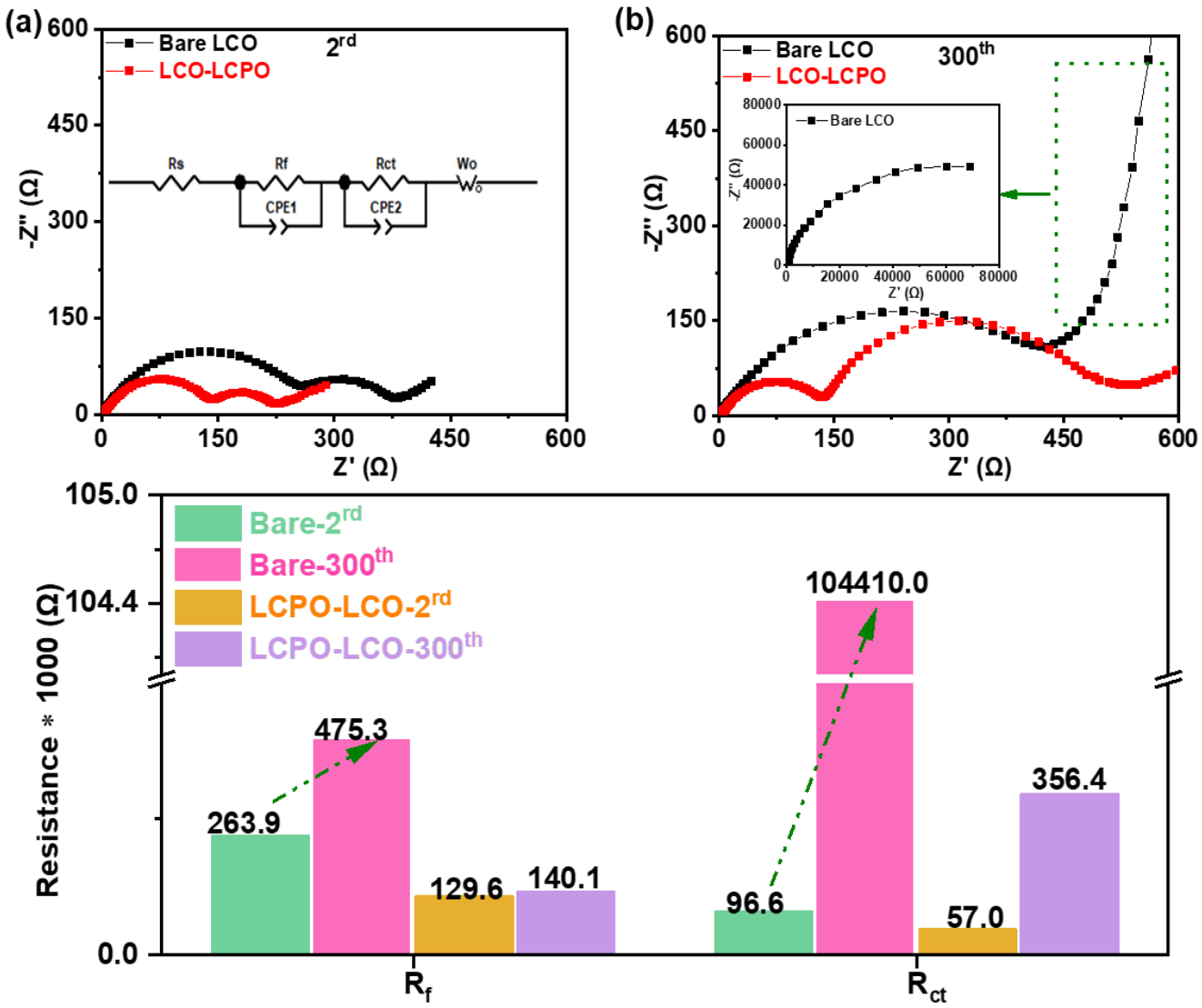
Electrochemical Performances of LCPO@LCO



✓ **LCPO-LCO, either at 30 ºC, 55 ºC, or-10 ℃, even ultra-high voltage such as at 4.7 V (*vs.* Li/Li$^+$) , they all exhibit excellent electrochemical performances**

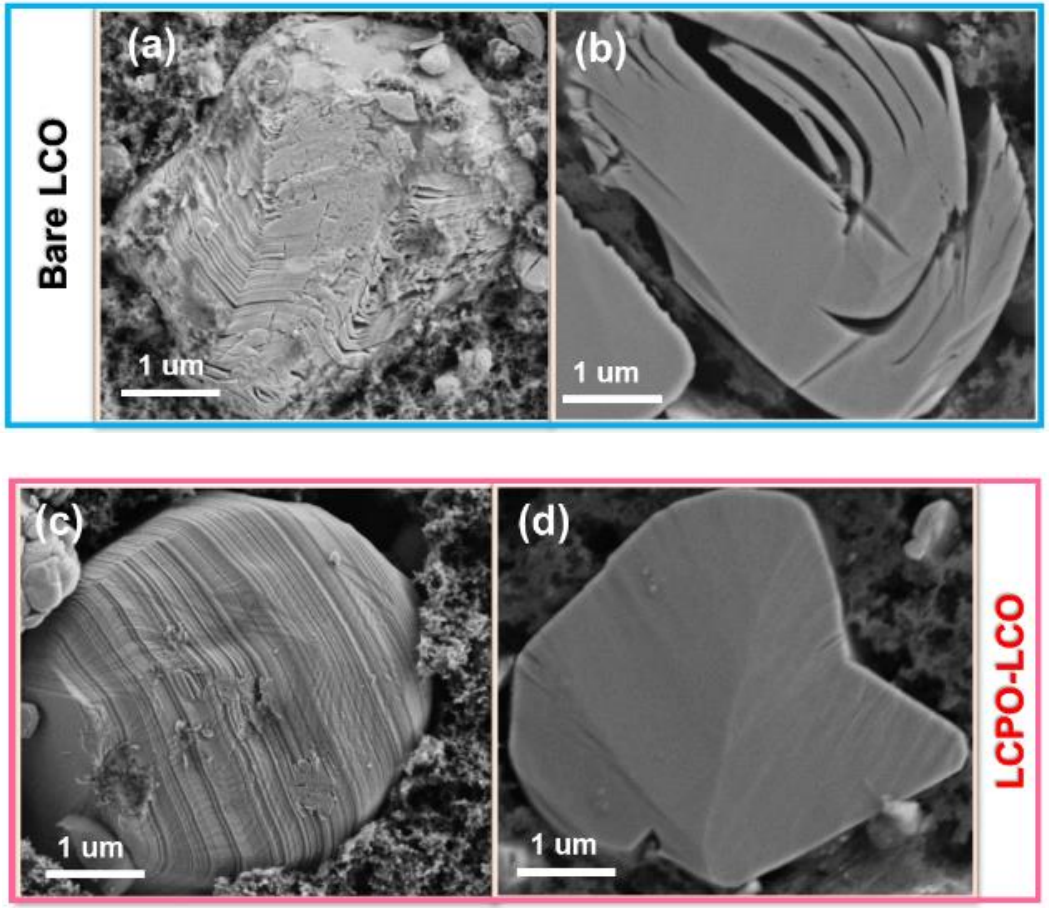
Electrochemical Impedances of LCPO@LCO

- EIS



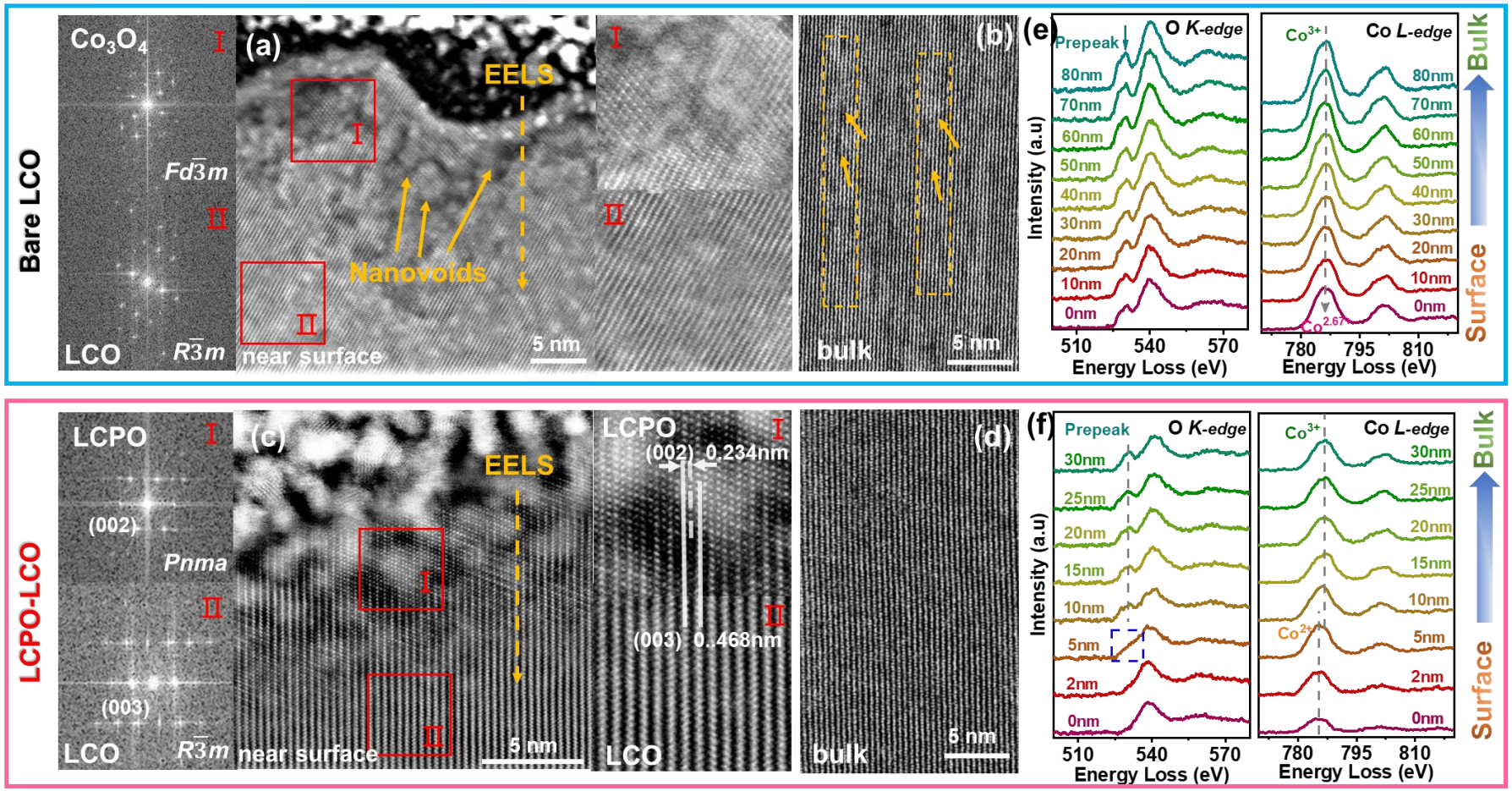
✓ LCPO coating can efficiently stabilize the Surface/interfacial structure of LCO

缓解微观结构退化-SEM



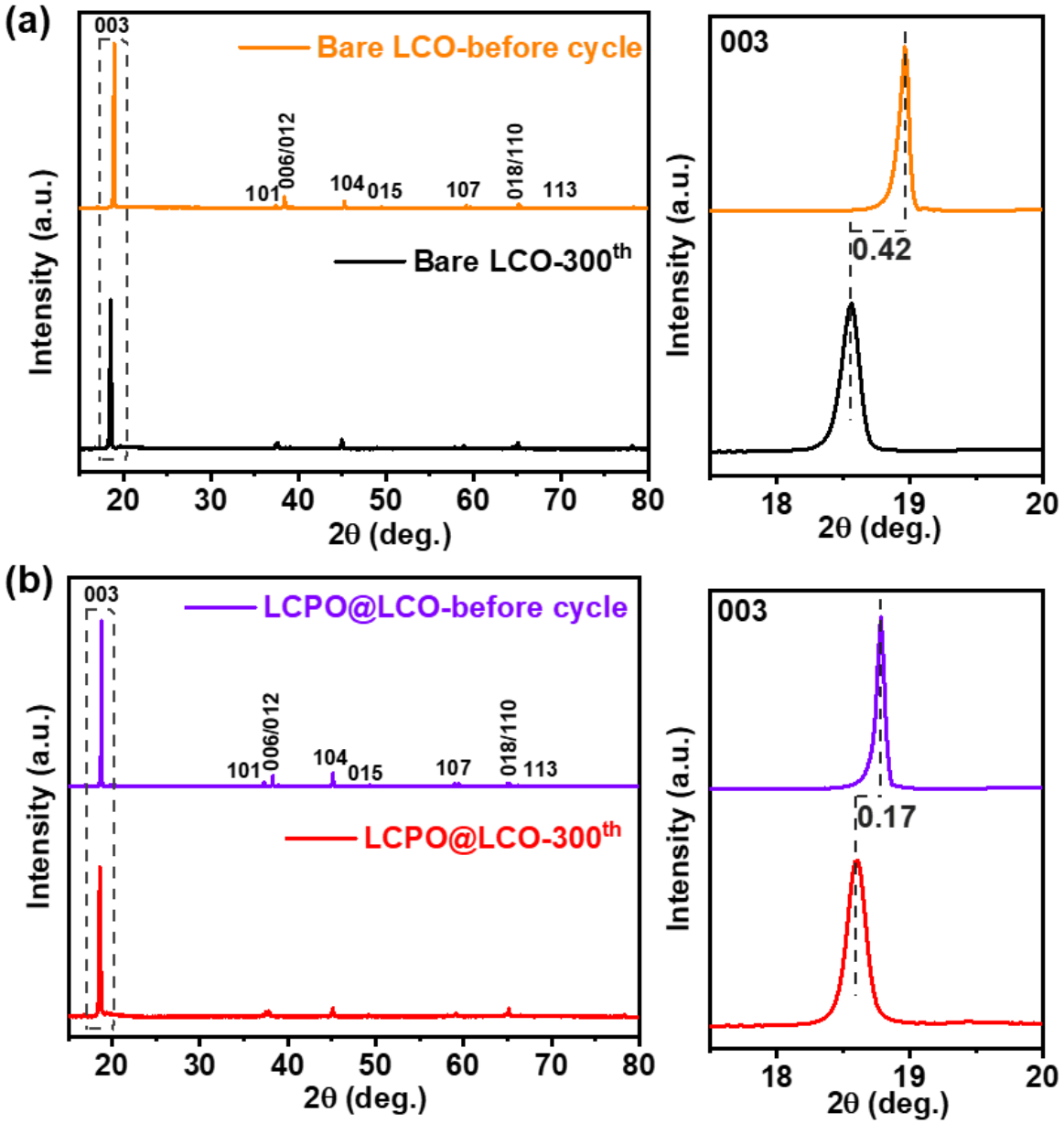
✓ 未包覆的LCO颗粒在长循环后产生了**严重的结构滑移和内部裂纹**，且表面可以观察到有破裂的颗粒碎片，这主要是**H1-3相变**所**产生的**较大的**不均匀应力**造成的

缓解微观结构退化-STEM&EELS



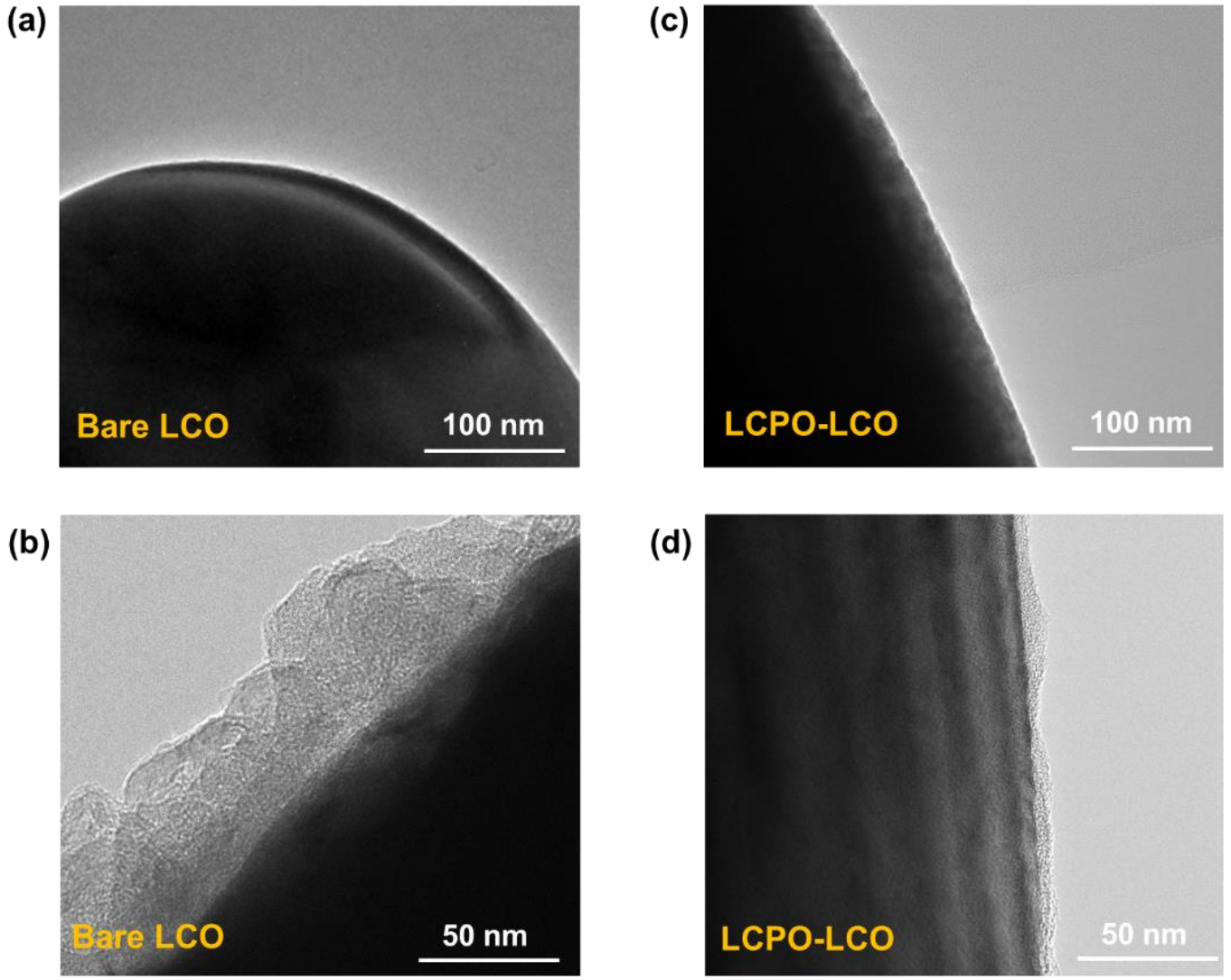
- ✓ **纳米空穴**的形成**主要是**循环中的**O损失和Co溶出造成**的。而O损失和Co溶出又会反过来诱导结构的不可逆转变
- ✓ **Co的迁移会**直接**降低晶格O的稳定性**，导致更多氧空位的形成，加速向LCO颗粒内部延伸。
- ✓ 循环后的LCPO包覆层仍然很好的粘附在LCO表面，没有**明显的晶格失配形成的裂缝**，有力地支持了该共晶格结构的循环耐久性
- ✓ 10nm处，O 2p轨道和Co 3d轨道之间的杂交作用的削弱主要归因于受**强的P-O共价键**的影响，**使得界面处O的电子云偏向于P元素，进而削弱了Co-O键的杂化强度**，使得LCO表面O的活性被降低。

缓解微观结构退化-XRD



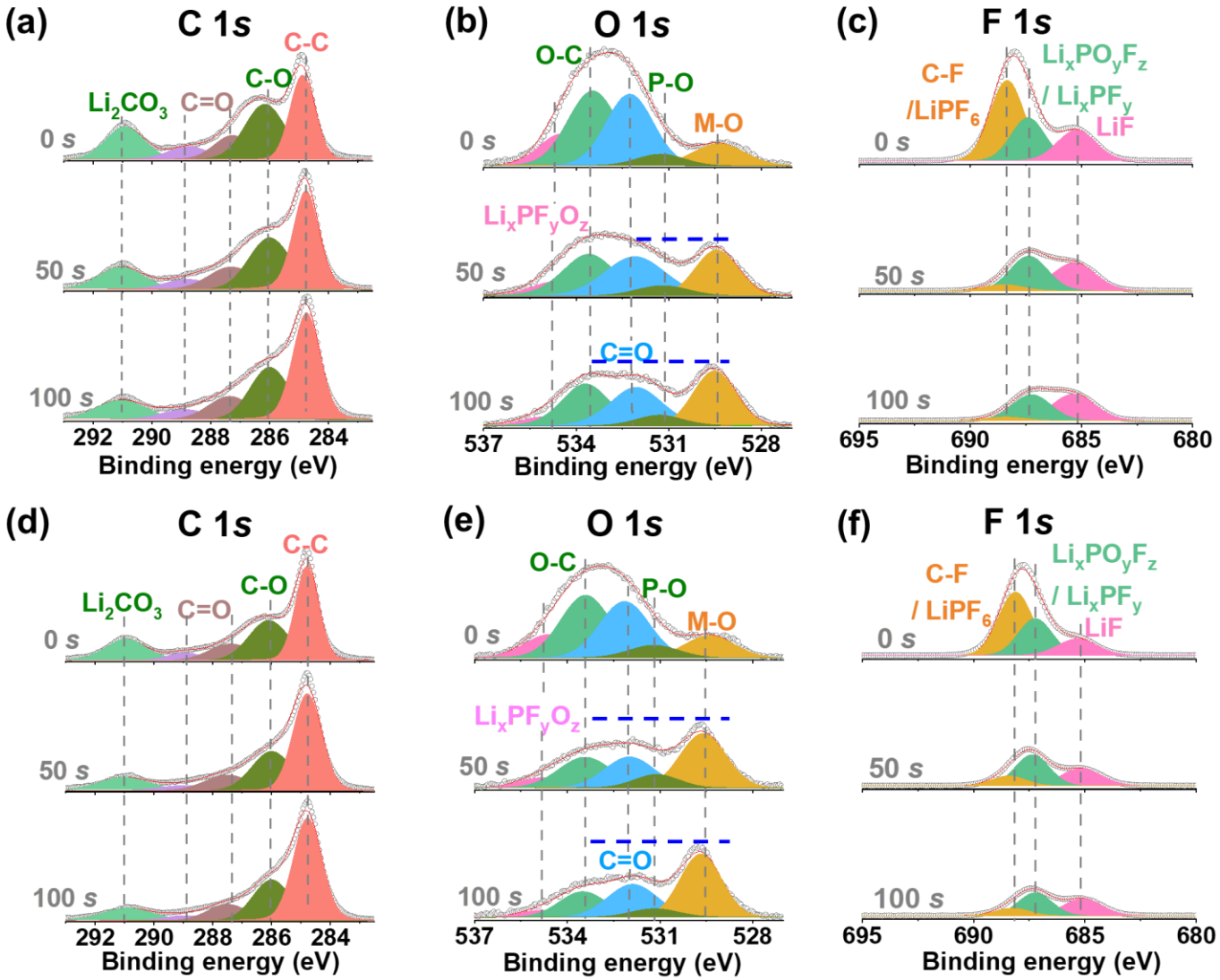
- ✓ 在300次循环后，未包覆LCO的(003)峰偏移0.42°明显高于LCPO-LCO（0.17°），表明**包覆LCPO后**，可以缓解LCO在循环过程中的**不可逆结构降解**

LCPO包覆层对界面副反应的抑制作用-TEM



✓ 未包覆LCO表面上覆盖了厚度超过50 nm的CEI层，这主要是由电解液的不受控分解引起的。对比之下，**LCPO-LCO可以显著抑制电解液分解，展现出薄的CEI层。**

LCPO包覆层对界面副反应的抑制作用-XPS



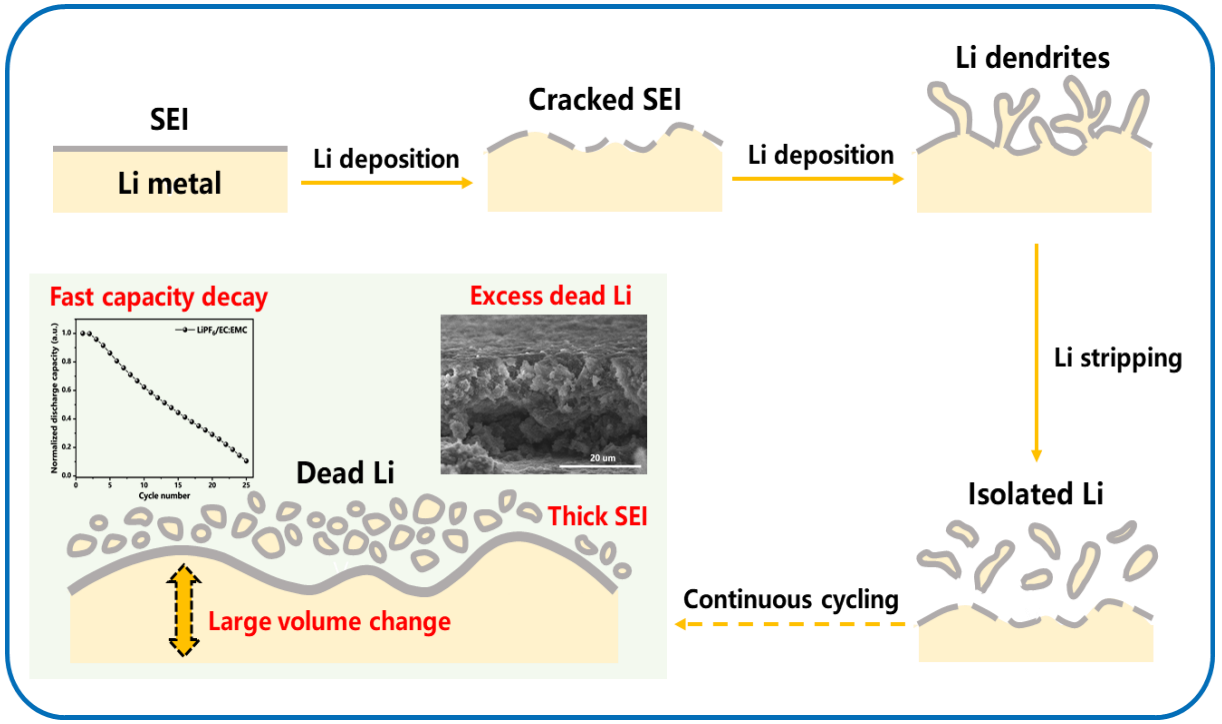
- ✓ **未包覆的LCO**表面$Li_xPF_yO_z$、**LiF和C=O、C-O峰的强度**明显**高于LCPO-LCO**，且M-O信号强度在刻蚀深度达到100 s之前，都是低于表面副产物信号强度的

Overview of Rechargeable Lithium Metal Anodes

Two main obstacles of lithium metal anodes:

- lithium dendrite growth
- low Coulombic efficiency

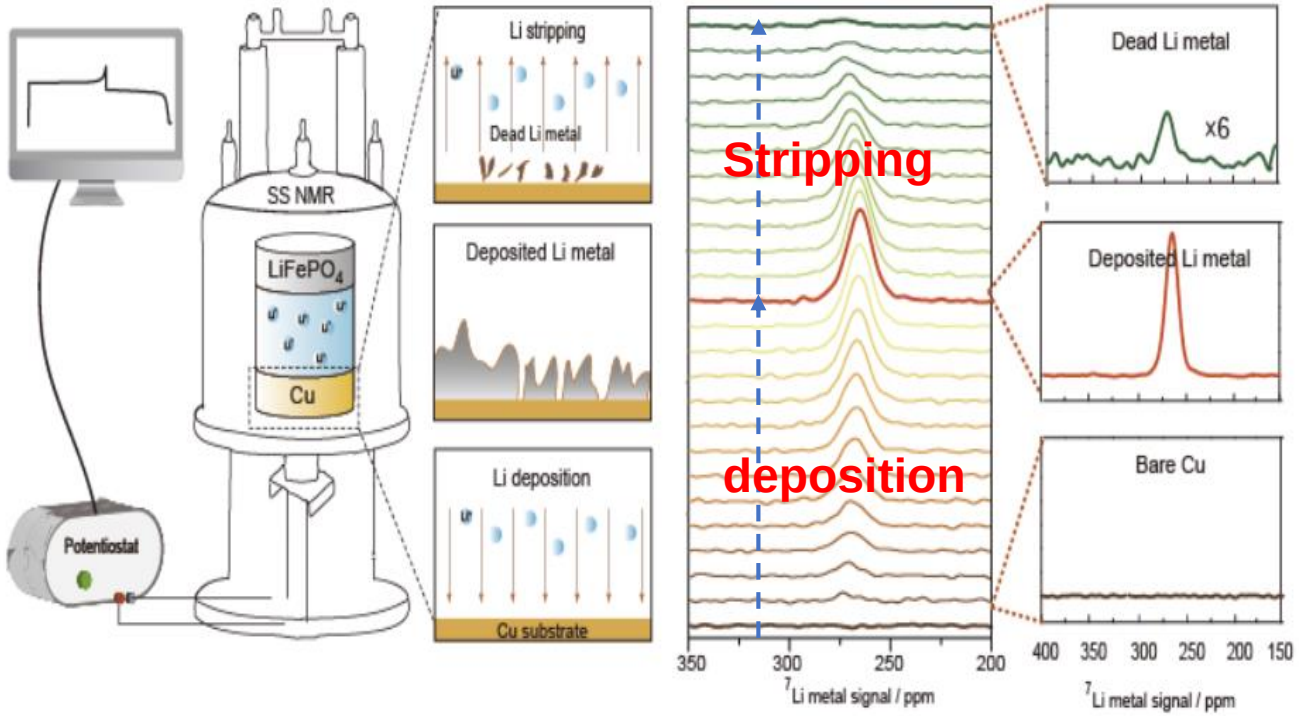
→ safety hazards and short cycling life

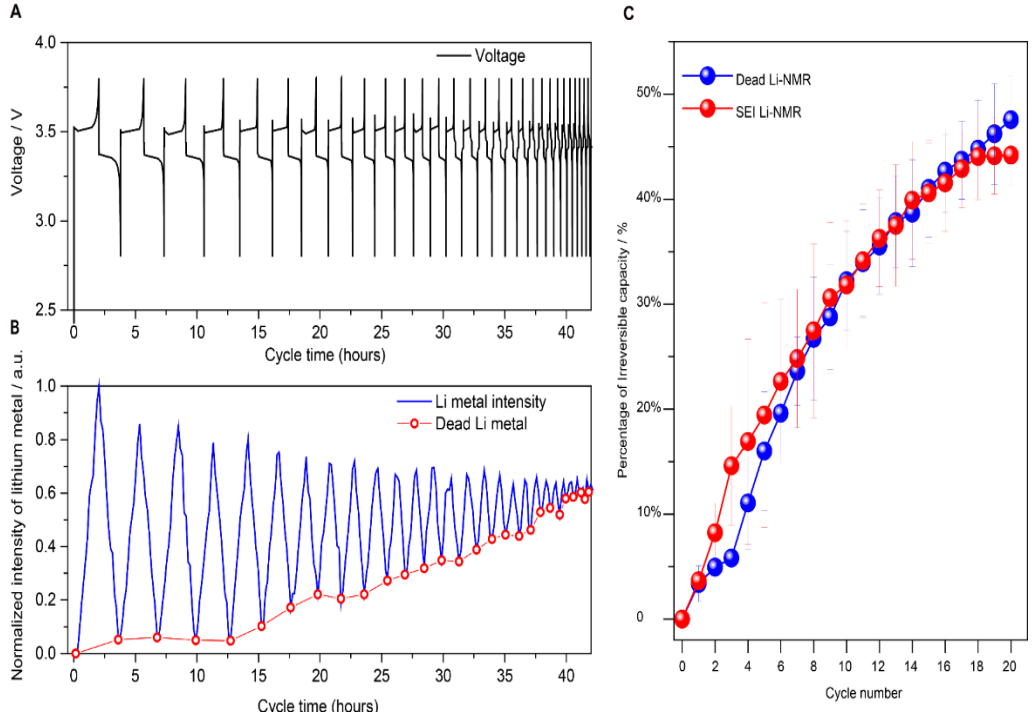


- Lithium tends to deposit in dendritic form
- lithium metal has almost infinite volume expansion due to the host-less characteristics
- The continuous cycling process leads to a consequent accumulation of inactive lithium

Electrochemical NMR Techniques for Battery Research

Advantages：Non-invasive、quantitative characterization of composition/bulk(local) structures during battery operation



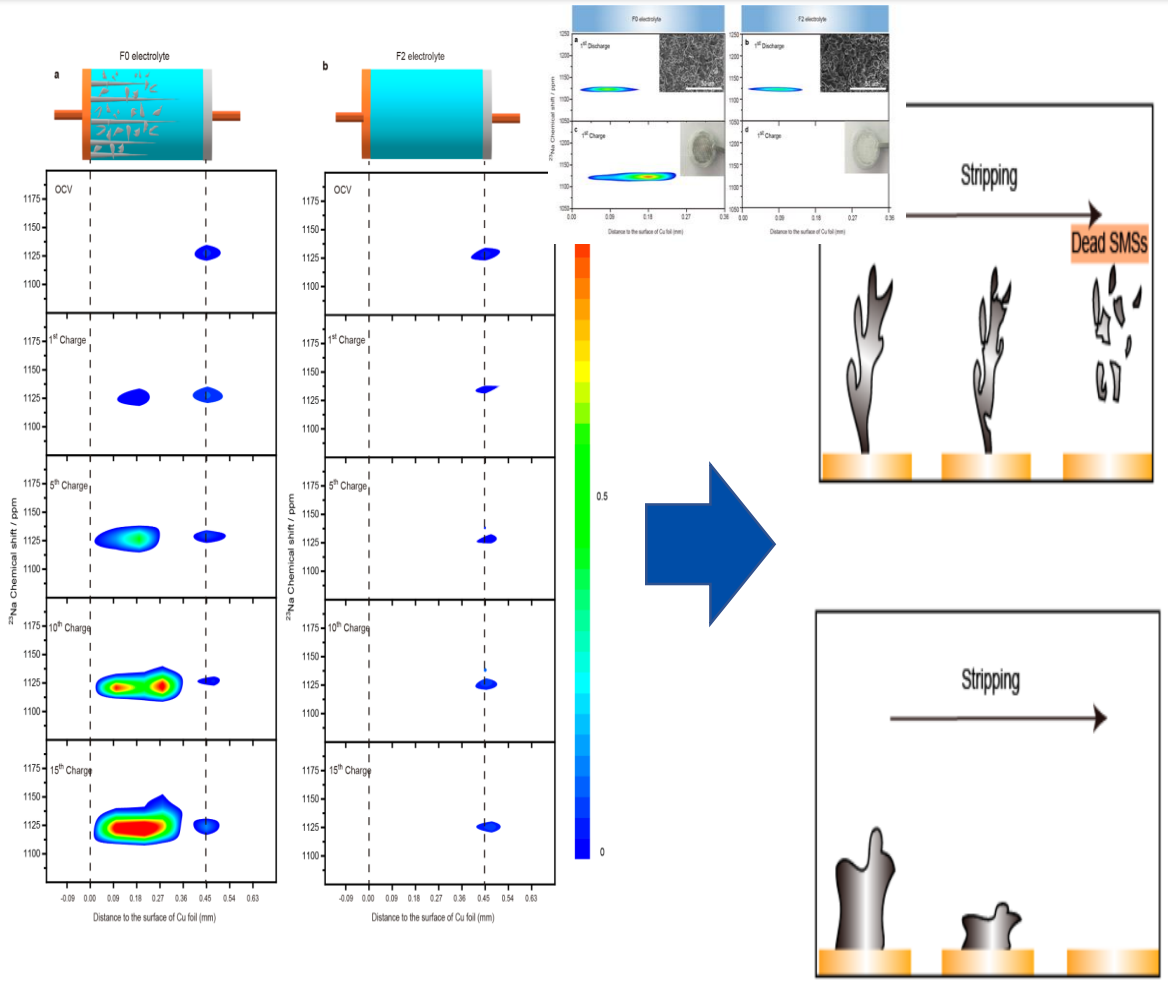


Irrev. Capacity = dead Li (NMR) + SEI compounds

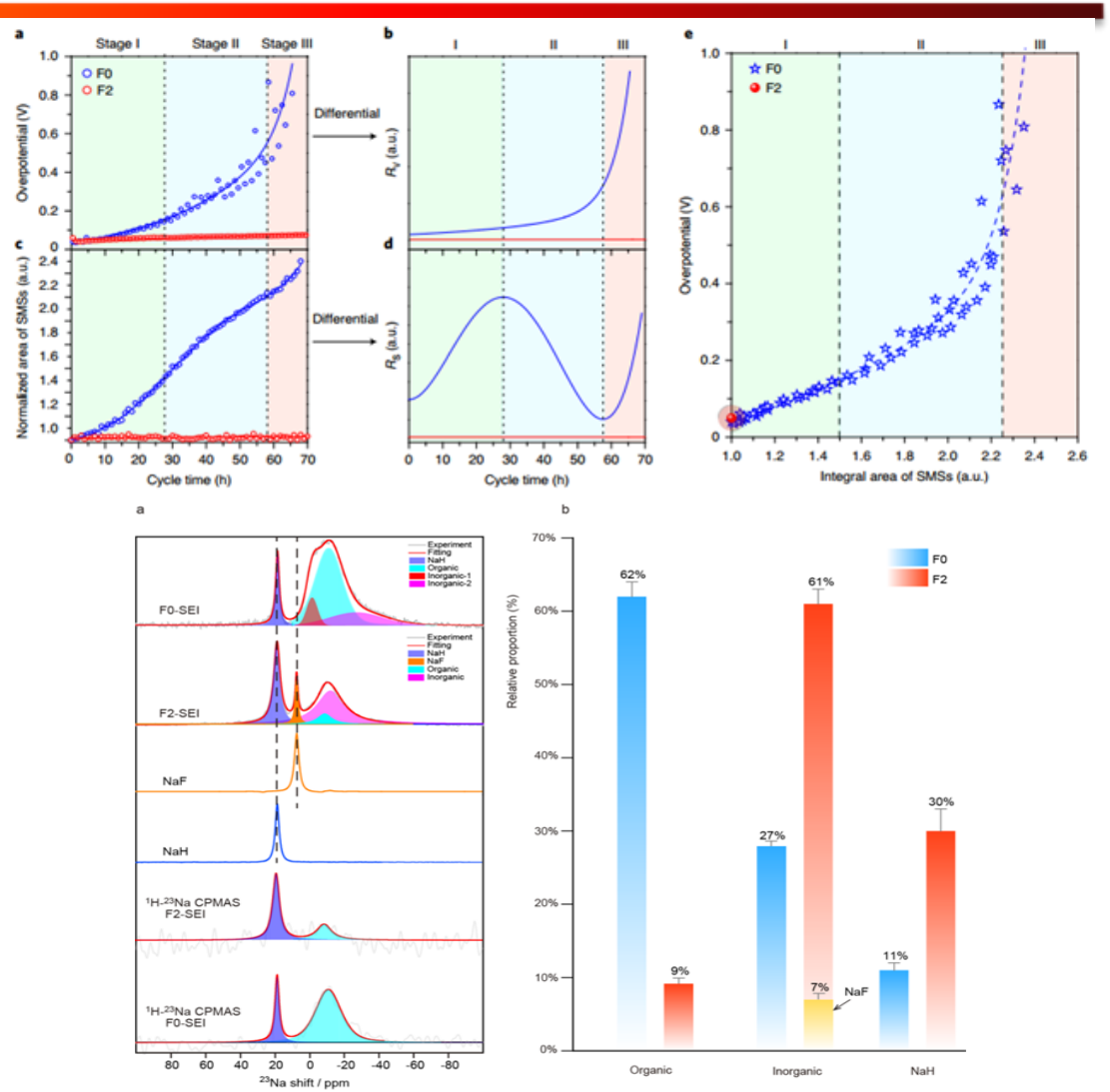
Differentiated dead Li metal during cycling, and realization of in-operando analysis of evolution of dead Li & SEI in anode-free cells

Y. Yang et al *Sci. Adv.* 2021, 7, eabj3423; *Adv. Mater.* 2021, 2005878

Operando Monitoring of Growth of Na dendrites by MRI techniques



Visualization of Na dendrites evolution during deposition/stripping processes



NaH was detected in the SEI of Sodium metal for the first time

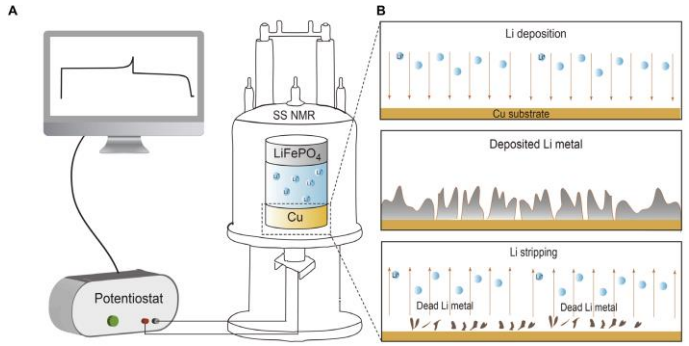
Y. Yang* et al; *Nat. Nanotechnol.* 2020, 15, 883

Recent works on Lithium Metal Anodes in My Group

Operando NMR technique

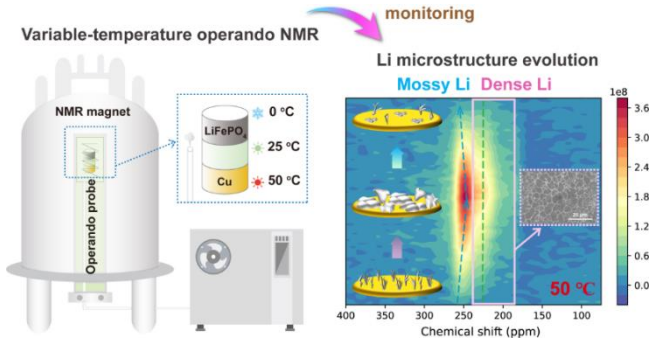
variable-temperature

Quantification of inactive lithium



Sci. Adv. 2021, 7, eabj3423.

Clarifying Li deposition/stripping behavior at different temperatures



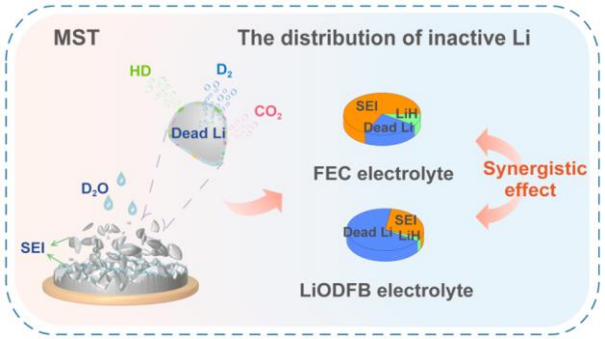
ACS Nano, 2023, 17, 24104-24114.

MST technique

some SEI species

LiH

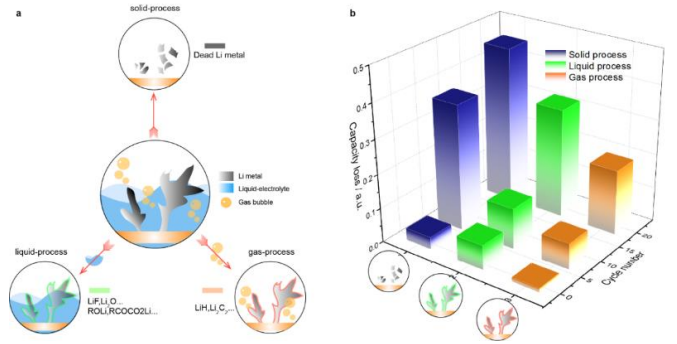
Quantifying the evolution of inactive Li/lithium hydride and their correlations



Nat. Commun. 2023, 14, 177.

LiH and Li_2C_2

Gas-induced inactive lithium formation



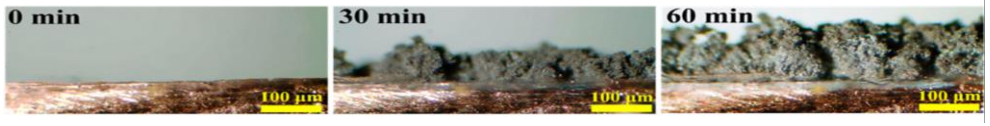
Nano Lett. 2022, 22, 6775-6781.

Recent works on lithium metal anodes in My Group

Operando optical microscopy

Visual observation of Li deposition

Baseline electrolyte



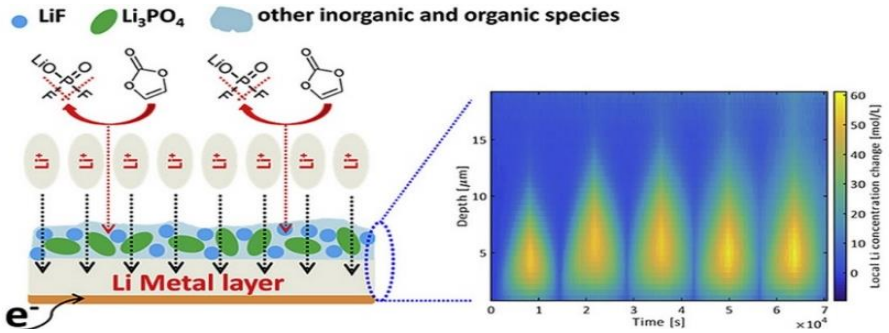
5 M-ETFEC electrolyte



ACS Appl. Mater. Interfaces 2020, 12, 27794−27802.

Operando NDP technique

The impact of different additives

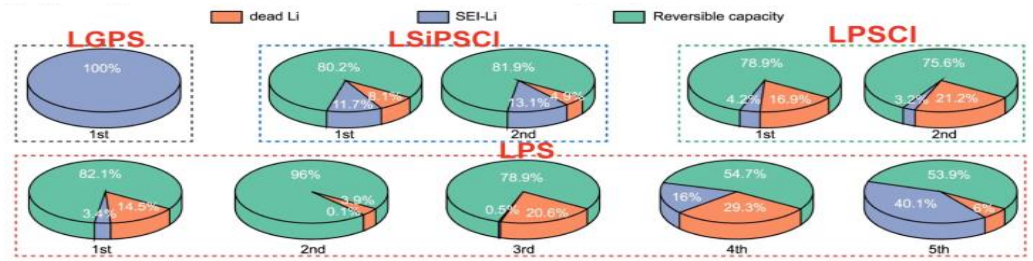


Energy Storage Materials, 2020, 29, 377-385.

All-solid-state lithium batteries

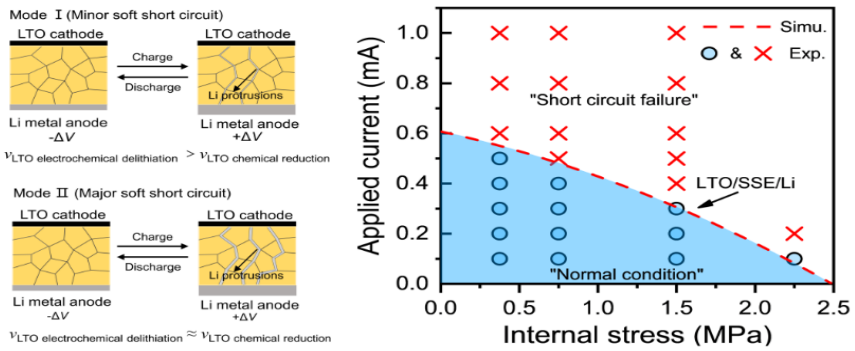
solid-state battery system

Quantification of inactive lithium in different sulfide-based solid electrolytes



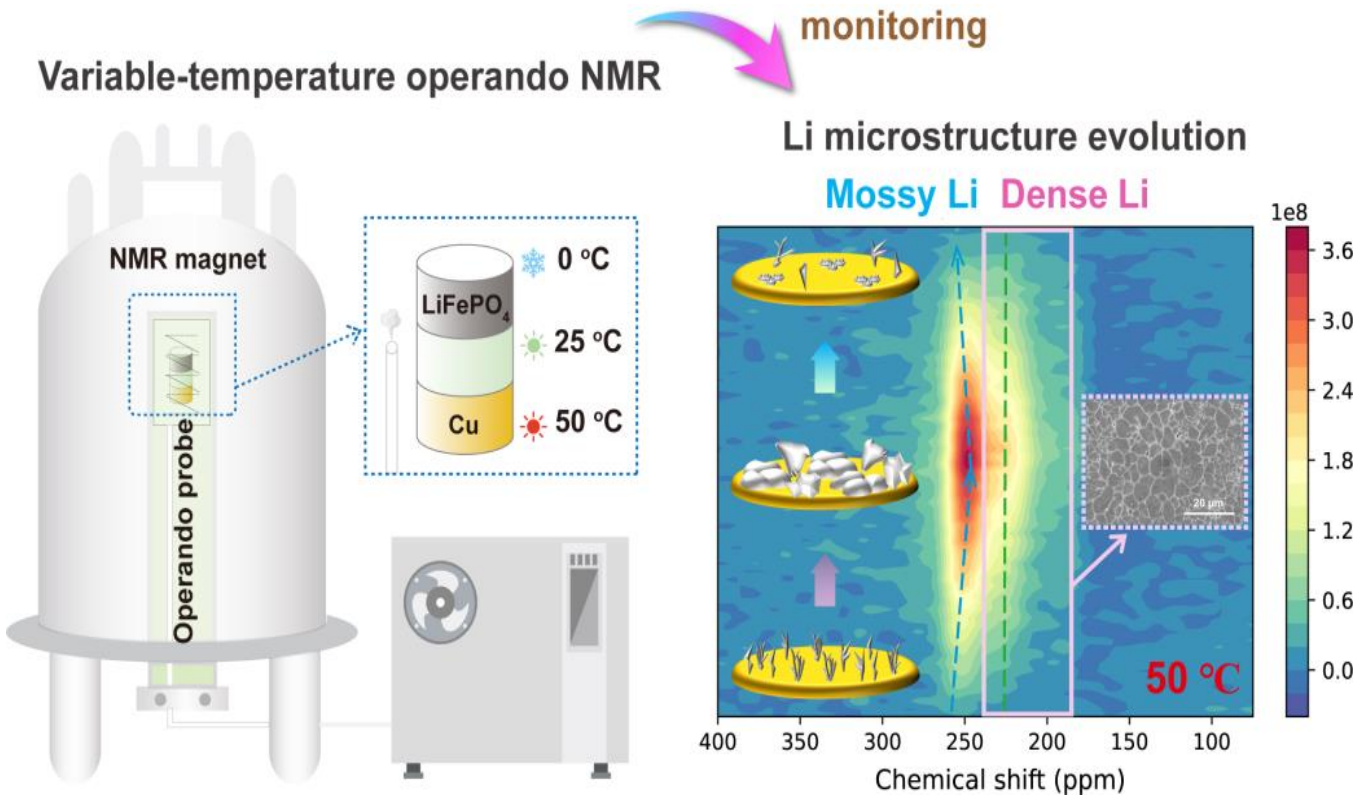
Nat. Commun. 2023, 14, 259.

Monitoring the stress evolution

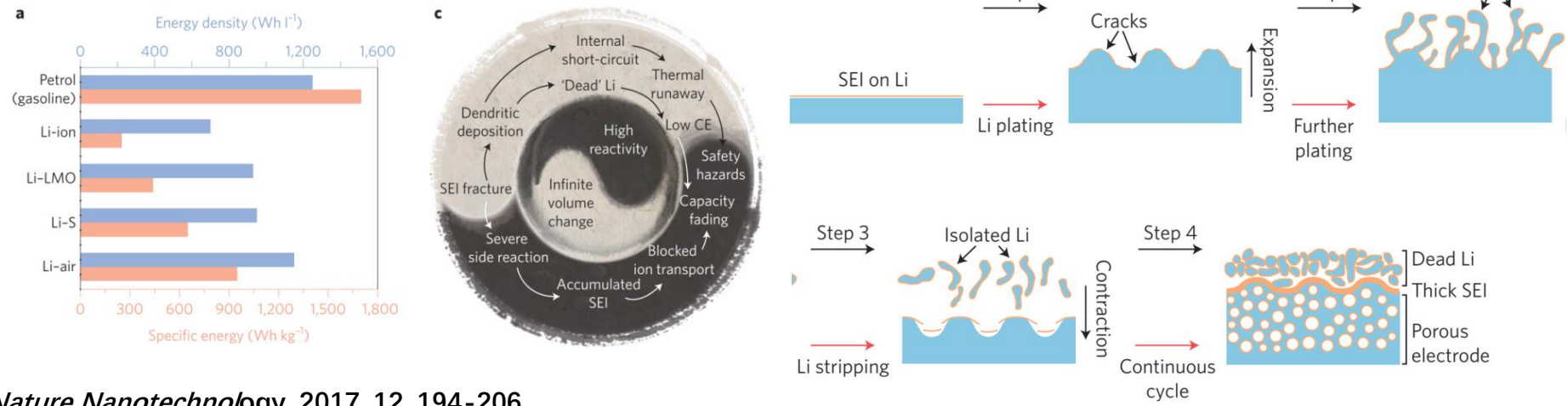


Adv. Energy Mater. 2023, 13, 2302643.

Clarifying the Temperature-Dependent Lithium Deposition/Stripping Process and the Evolution of Inactive Li in Lithium Metal Batteries

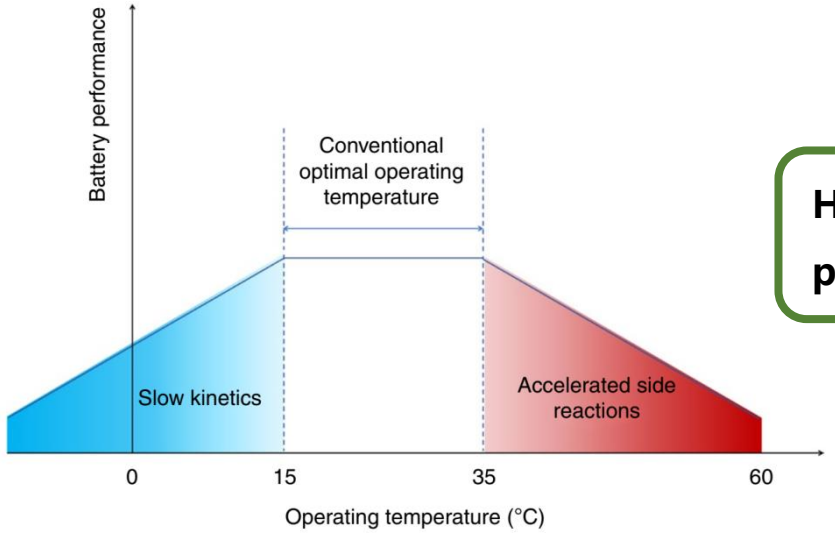


Rechargeable Lithium metal Anodes



*Nature Nanotechnol*ogy, 2017, 12, 194-206.

The uneven deposition/stripping process of lithium metal anode seriously affects the electrochemical reversibility and results in continuous formation of inactive lithium

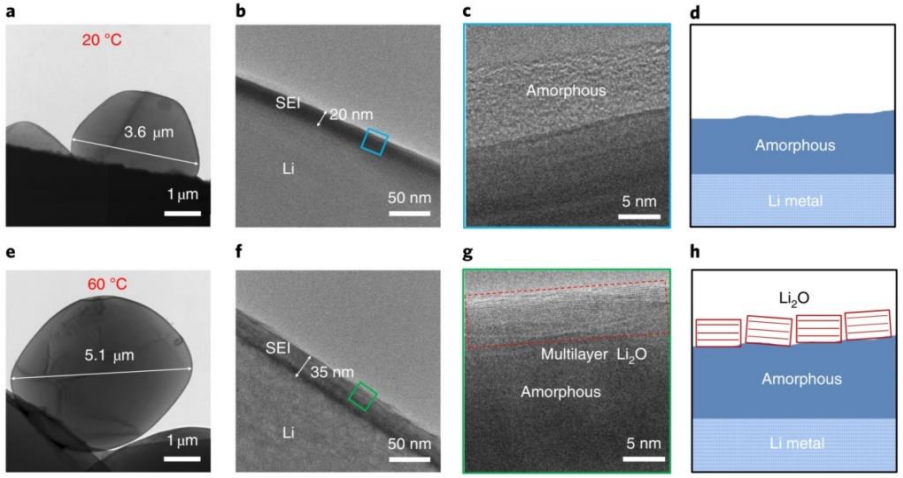


How operational temperature affects dynamic process occurring in lithium metal anodes?

The required operating temperature range is gradually expanding

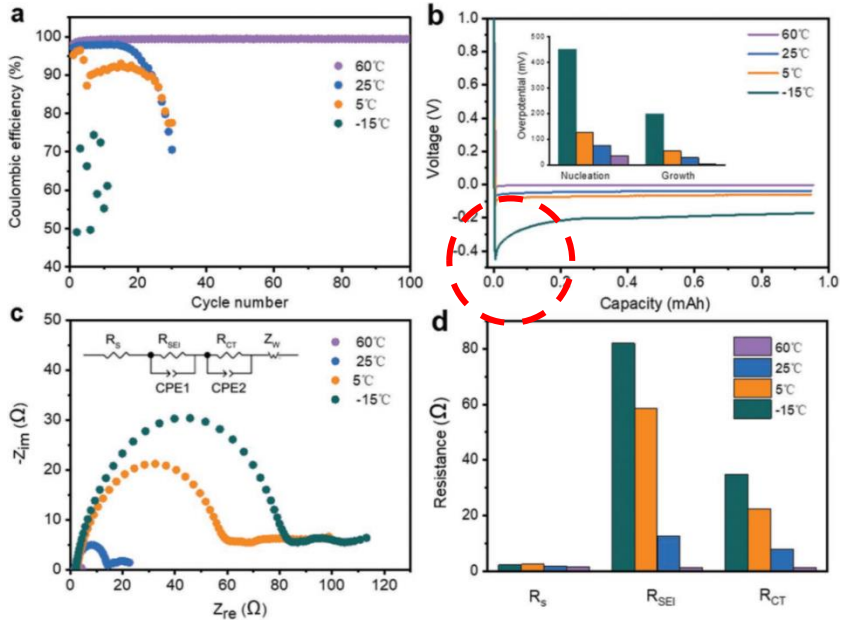
Nature Energy, 2019, 4 (8), 664-670.

Temperature effects

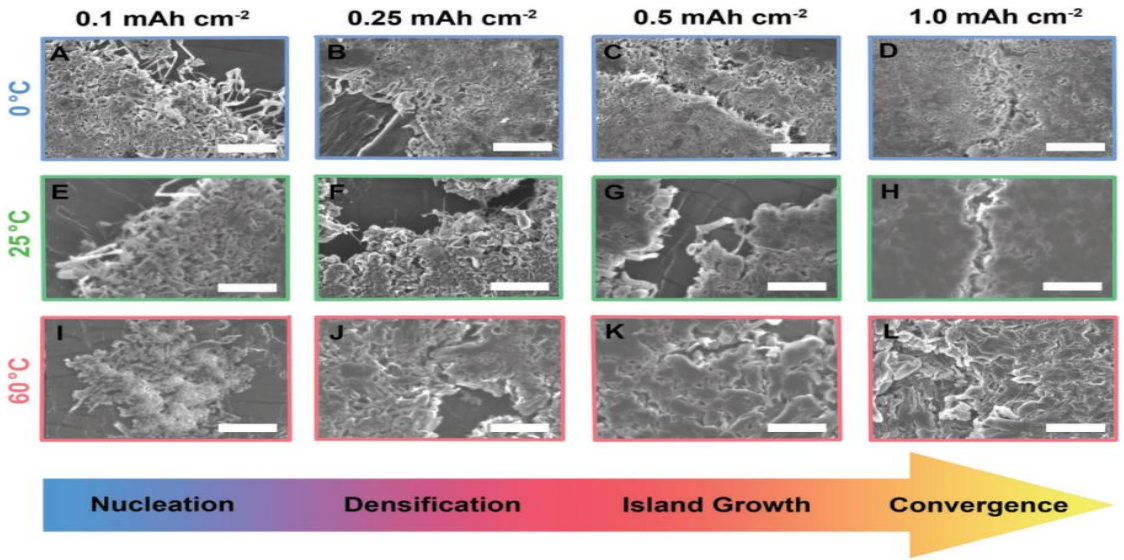


Nature Energy, 2019, 4 (8), 664-670.

Excellent SEI nanostructure at high temperature



Advanced Functional Materials, 2019, 29, 1904629.

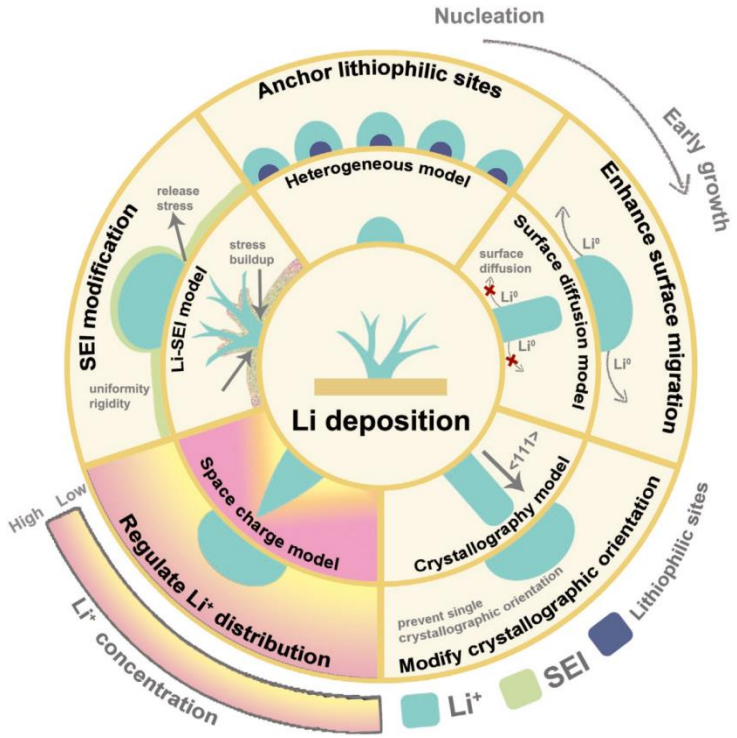


Different temperature leads to different nucleation overpotential

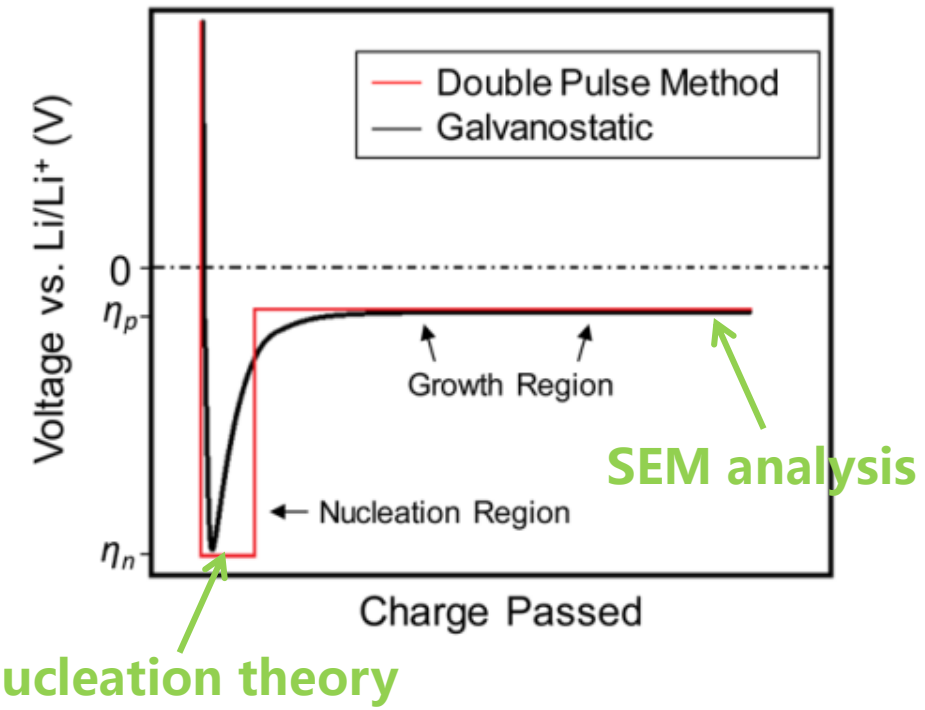
The final deposition morphology at different temperatures

Adv. Mater. 2020, *32*, 2002550

The nucleation and growth of Li metal



Adv. Mater. 2021, 33, 2004128

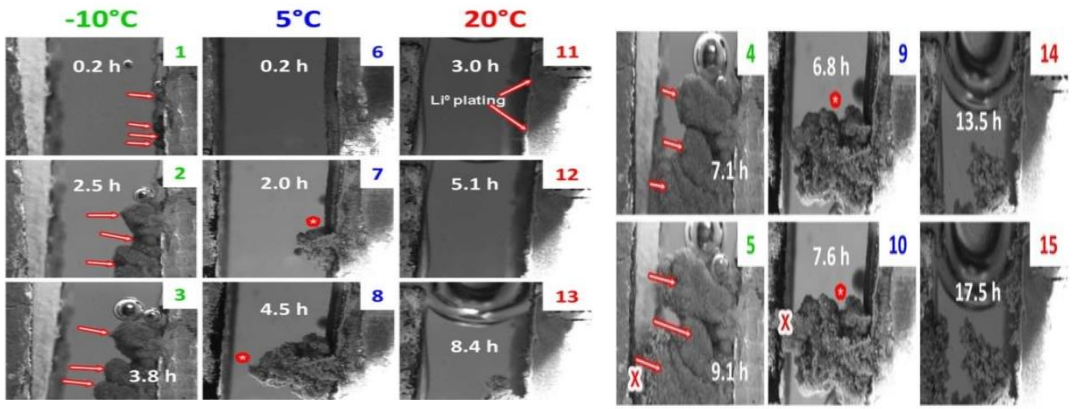


Nano Lett. 2017, 17, 1132-1139

- Nucleation theory focuses on the nucleation stage, while SEM analysis pays close attention to the final result of the growth stage
- It is still in sore need of operando technique to study the whole process of lithium deposition under variable temperatures

Operando variable-temperature techniques

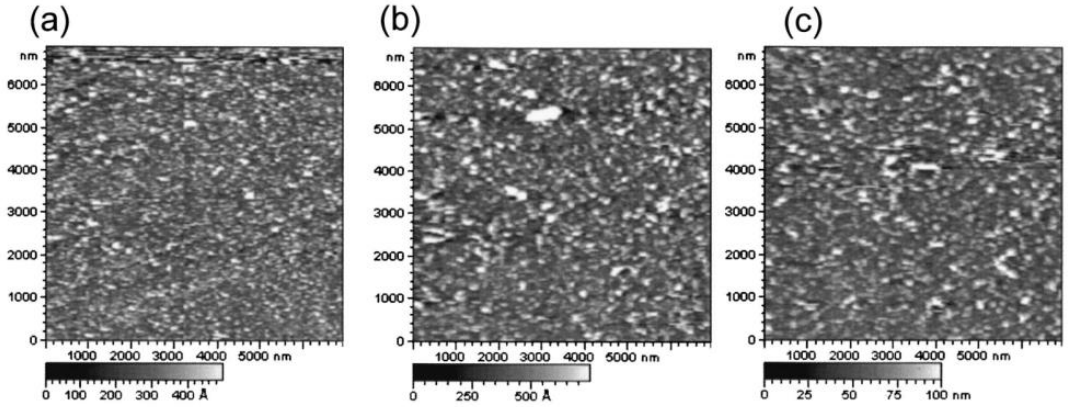
Optical microscopy



- **Poor resolution**
- **No stacking pressure**

ECS Electrochemistry Letters, 2015, 4, A24-A27.

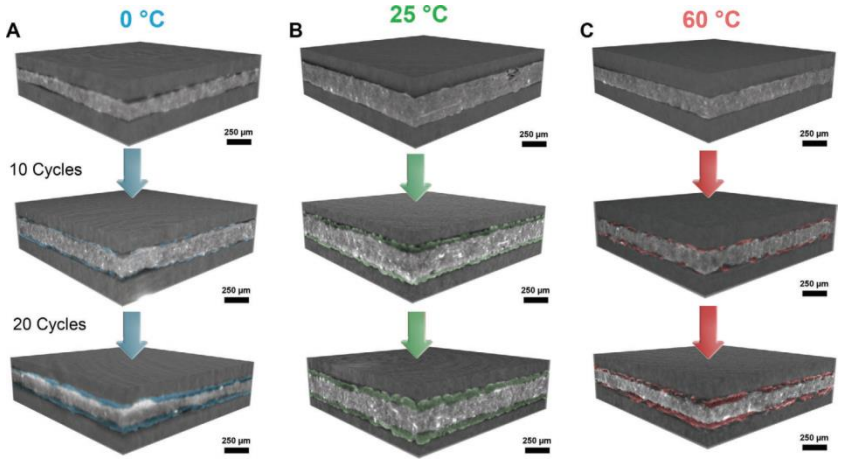
Atomic Force Microscopy



- **Only surface information**
- **Without applied pressure**

Journal of The Electrochemical Society, 2002, 149, A385-A390.

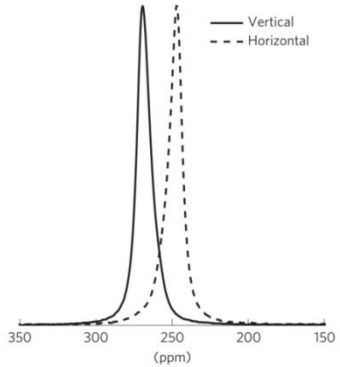
Synchrotron X-ray computed tomography



- **X-ray is not sensitive to light elements**
- **Only observe macroscopic morphological evolution**

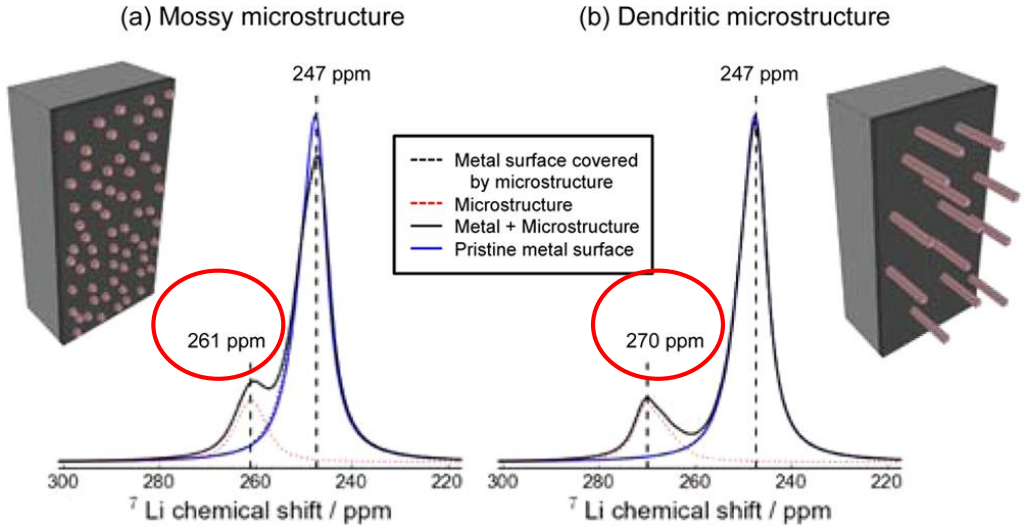
Adv. Mater. 2020, 32, 2002550.

Operando NMR technique for Li Metal Studies

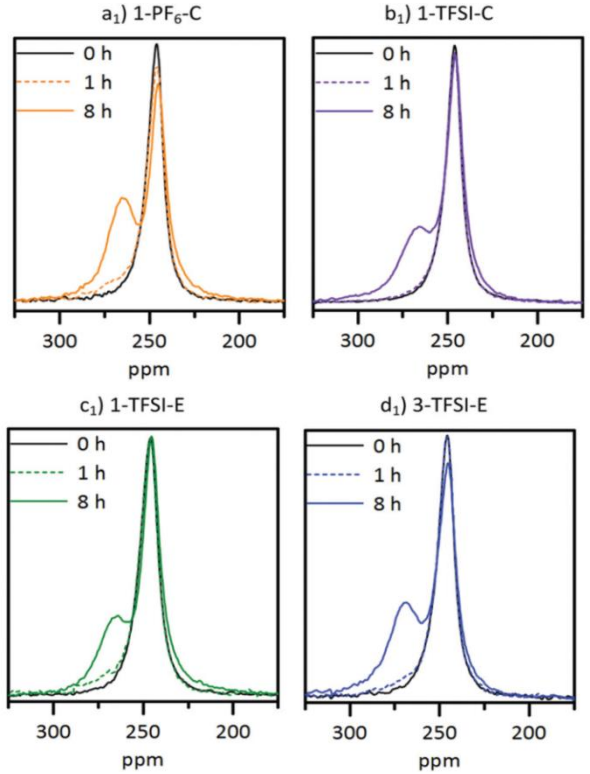


Nature Materials, 2010, 9 (6), 504-510

The chemical shift of lithium metal is highly sensitive to the orientation and morphology



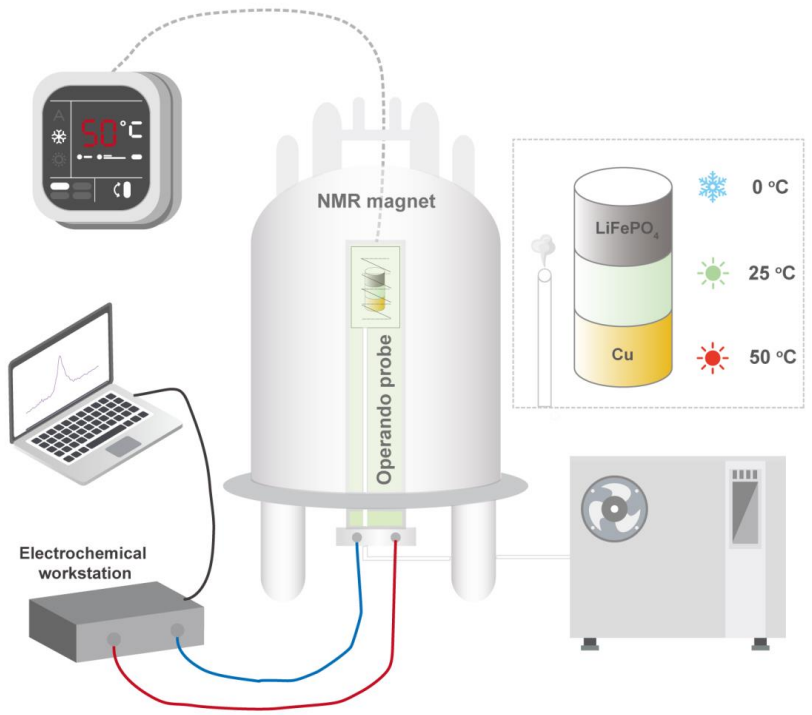
J. Phys. Chem. C, 2015, 119, 16443-16451



Phys. Chem. Chem. Phys., 2019, 21, 26084--26094

✓ **Dynamically monitor the evolution of different lithium microstructures**

Operando Variable-Temperature NMR





We develop an operando variable-temperature probe which can achieve precise temperature control (± 0.3 °C) by blowing air flow with different temperatures into the probe

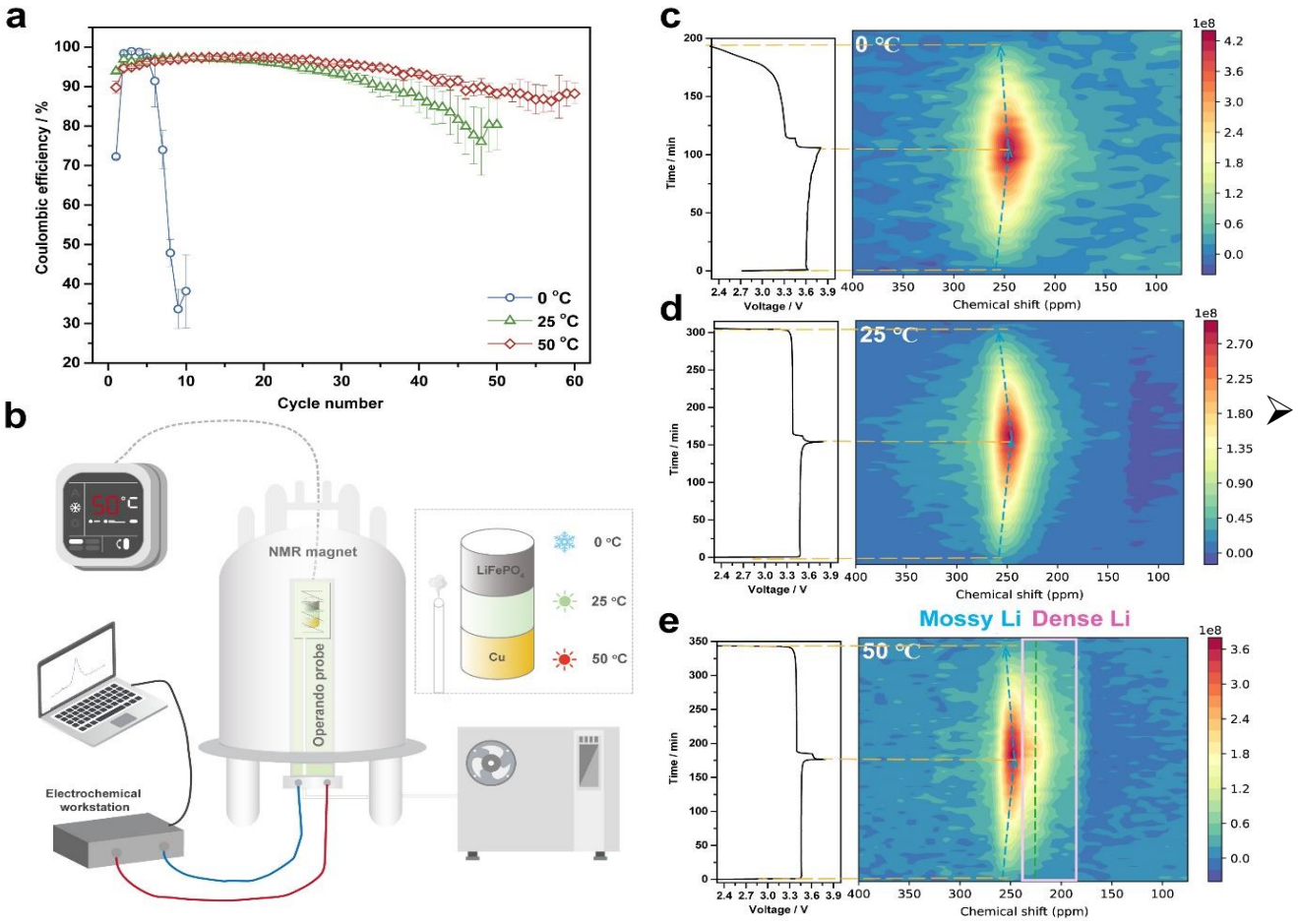
To elucidate the effect of temperature on the deposition/stripping of lithium metal anodes

Deposition/stripping behavior at different temperatures

Operando variable-temperature NMR

$LiFePO_4$||Cu operando cell

1 M LiODFB in EC/EMC electrolyte

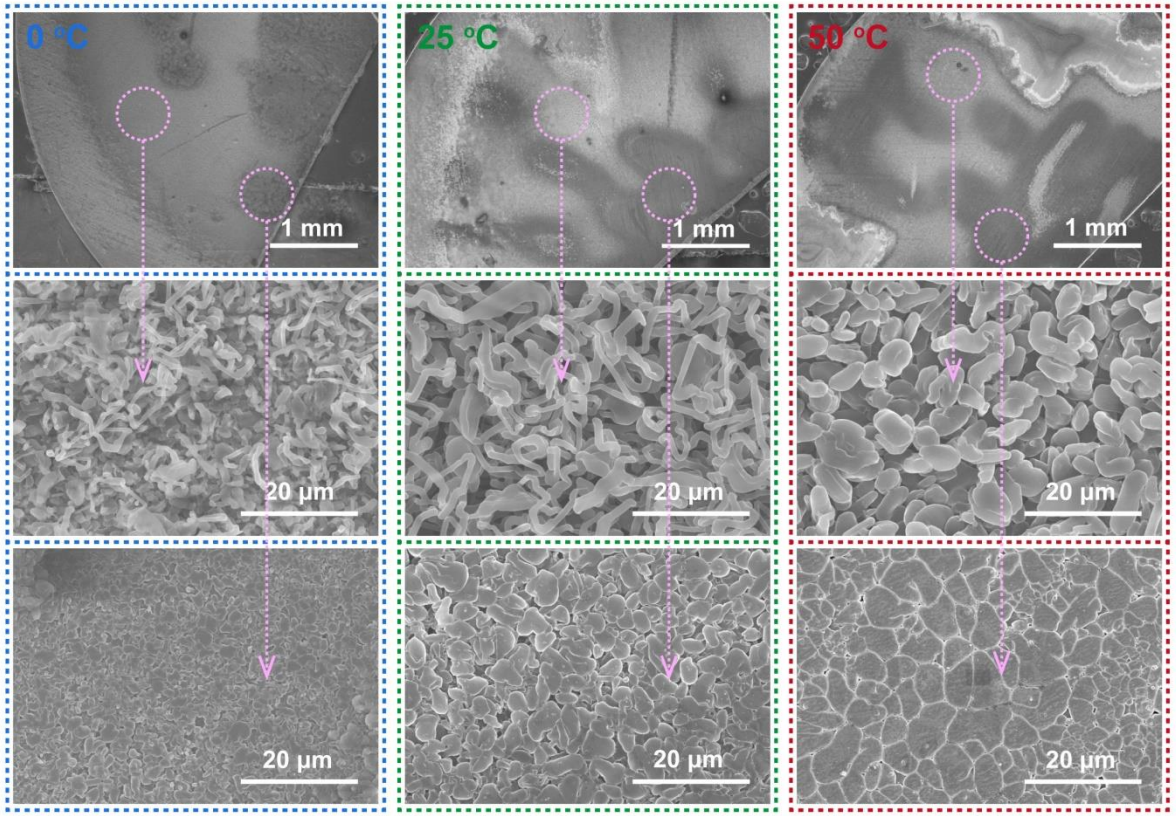


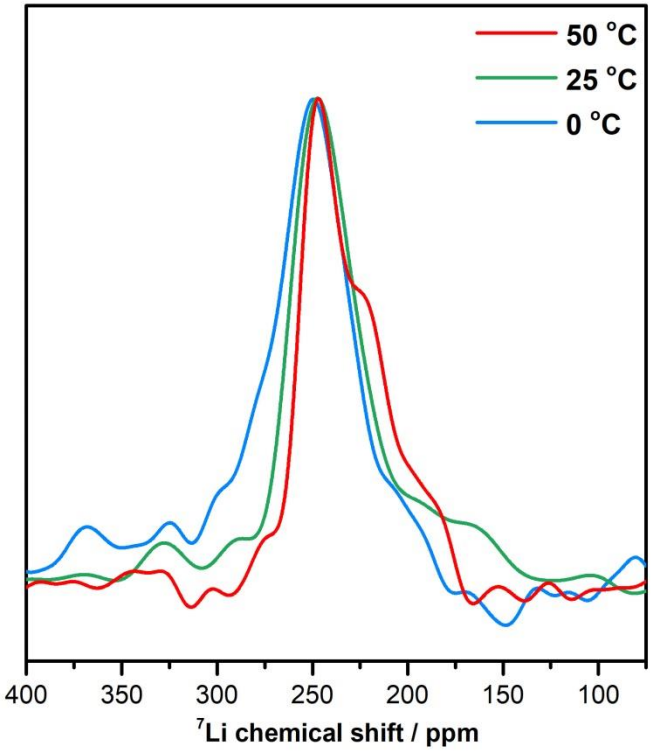
- The initial chemical shifts are all around 260 ppm — newly deposited Li metal is mossy/dendritic-like
- In the deposition process, chemical shift gradually moves towards the direction of higher field (lower chemical shift) — the transverse growth rate of lithium deposits is greater than the longitudinal growth rate (lithium metal fattening)

At 50 °C, a signal with low chemical shift (~ 223 ppm) which is absent at 0 °C and 25 °C appears → **dense lithium deposits**

The morphological evolution of Li microstructure at different Temp.

SEM

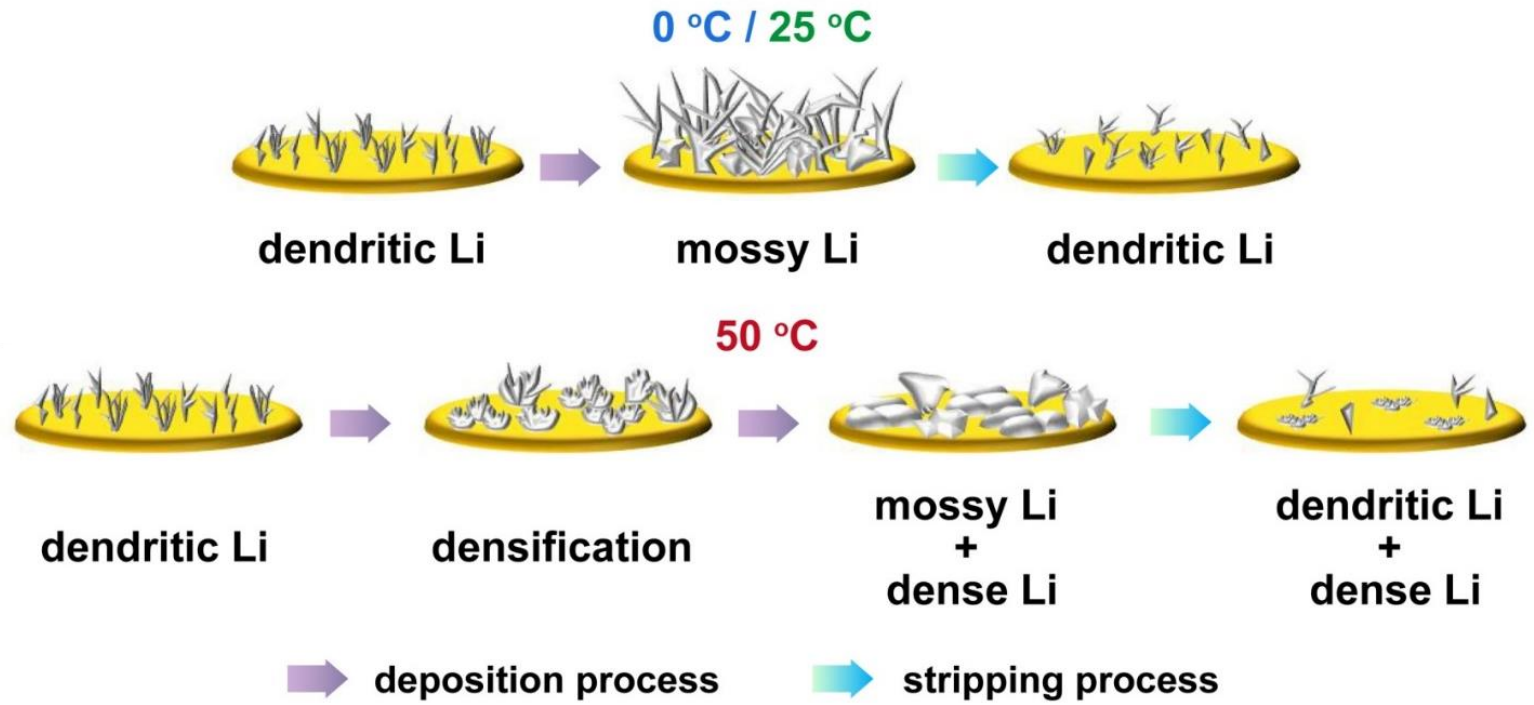




Our operando variable-temperature NMR results can be in well accordance with the actual morphology of lithium deposits monitored by SEM

The morphological evolution of Li microstructure at different Temperature

The deposition/stripping behavior of lithium metal in carbonate electrolyte at different temperatures:



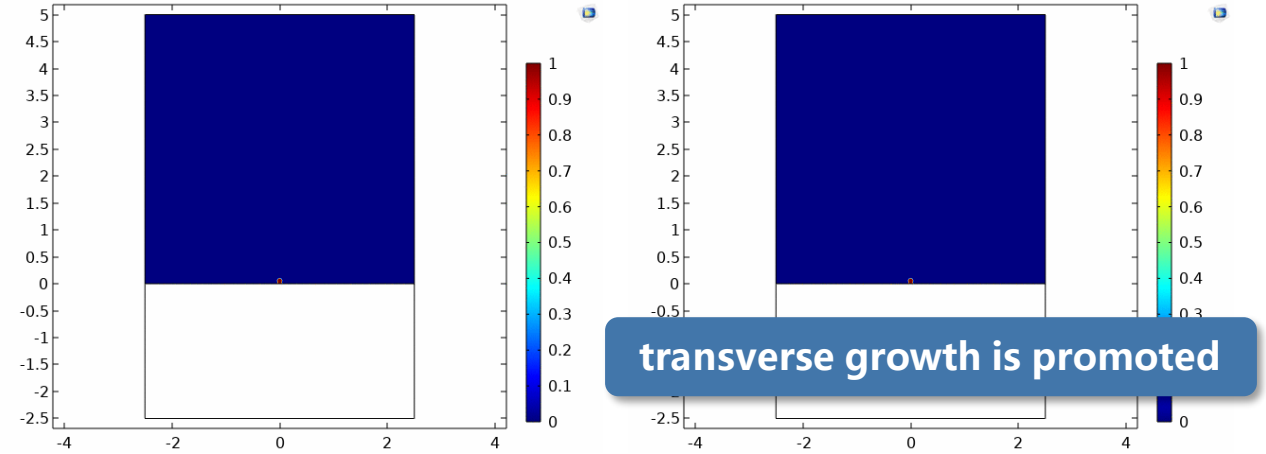
- ✓ At 0 °C and 25 °C, there is a **similar evolution pattern.**
- ✓ At 50 °C, **partial densification occurs** during the dominant transverse growth, forming excellent dense phase morphology.

Impacts of temperature on the Li metal deposition

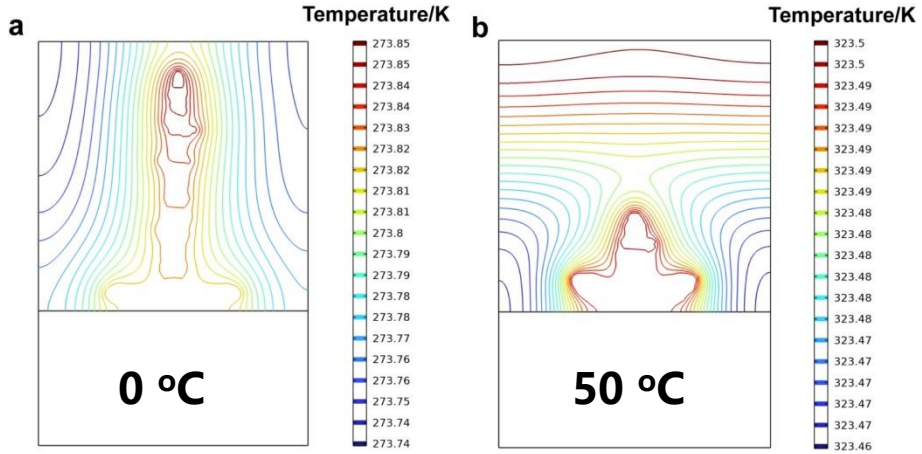
☐ Comsol simulation

Nonlinear phase-field coupled with heat-transfer model

0 ºC **50 ºC**



isothermal curves

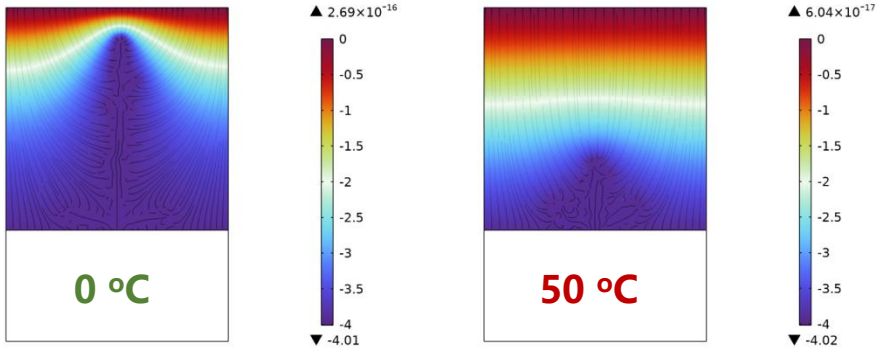


- **0 ºC — a temperature gradient from the tip of the deposited Li metal to the bulk**
- **50 ºC — temperature is uniformly distributed on the deposited Li metal surface without a bulk temperature gradient**

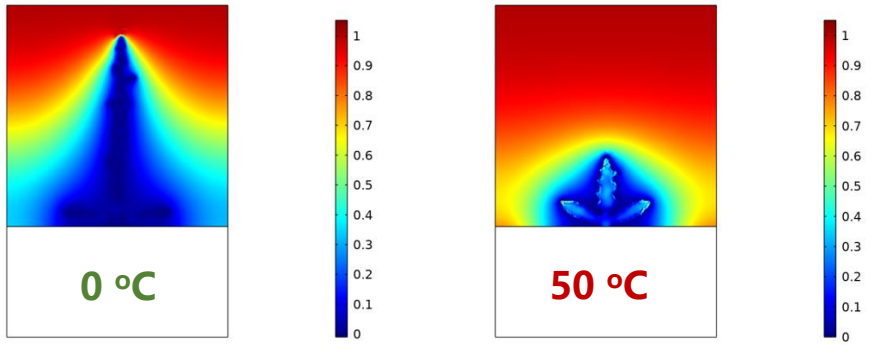
Impacts of temperature on the Li metal deposition

☐ Comsol simulation

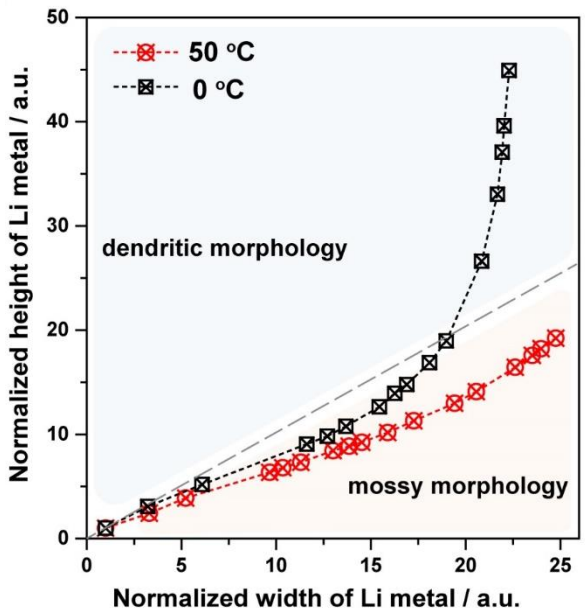
electric field distribution



Li^+ concentration distribution



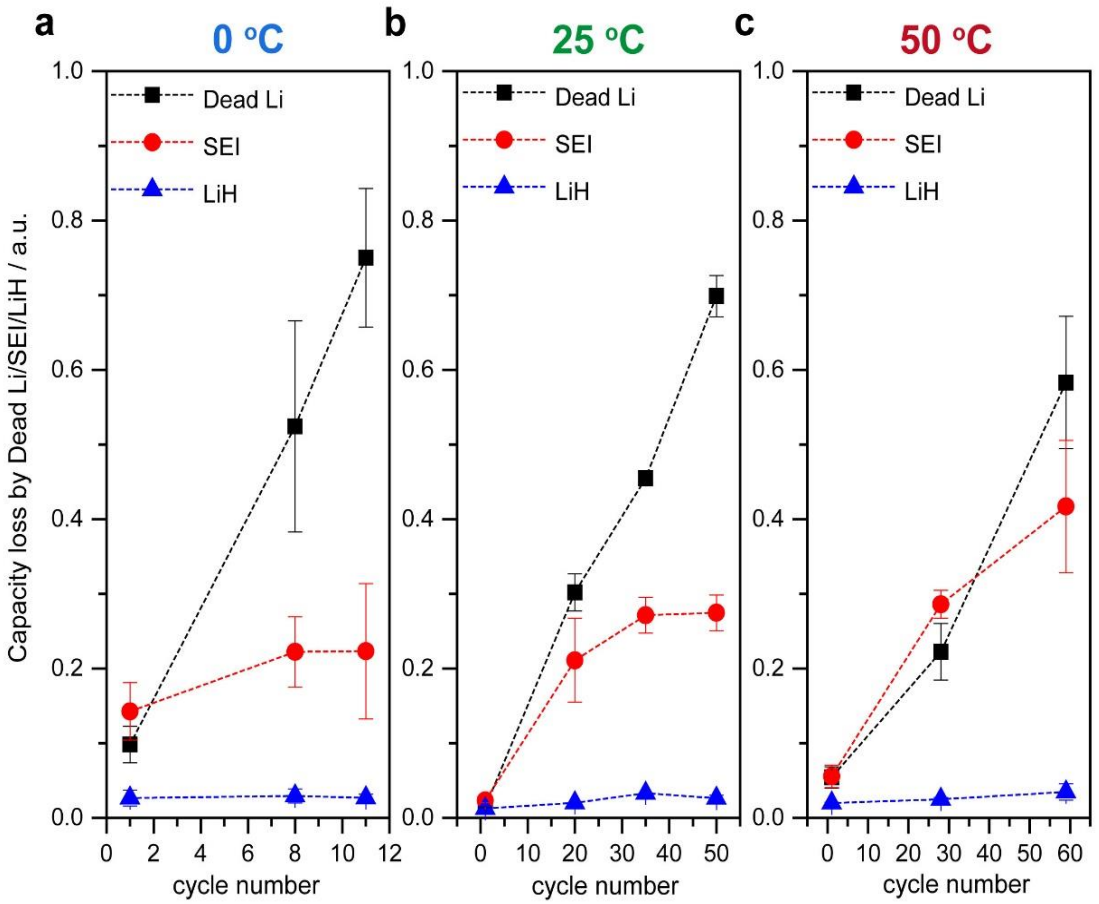
The evolution of dendrite width and height



At 0 °C — a highly uneven distribution of electric field and Li^+ concentration — the reason for promoting lithium dendrite growth

Quantitative analysis of inactive lithium

MST



- At 0 °C, dead Li metal occupies an absolutely dominant position in capacity loss, which is related to the atrocious dendritic morphology
- The preeminent morphology at 50 °C significantly reduces the formation of dead Li metal, but the intensified decomposition of electrolyte at high temperature giving rise to the generous formation of SEI

Performance-enhancing strategy of Li metal anode

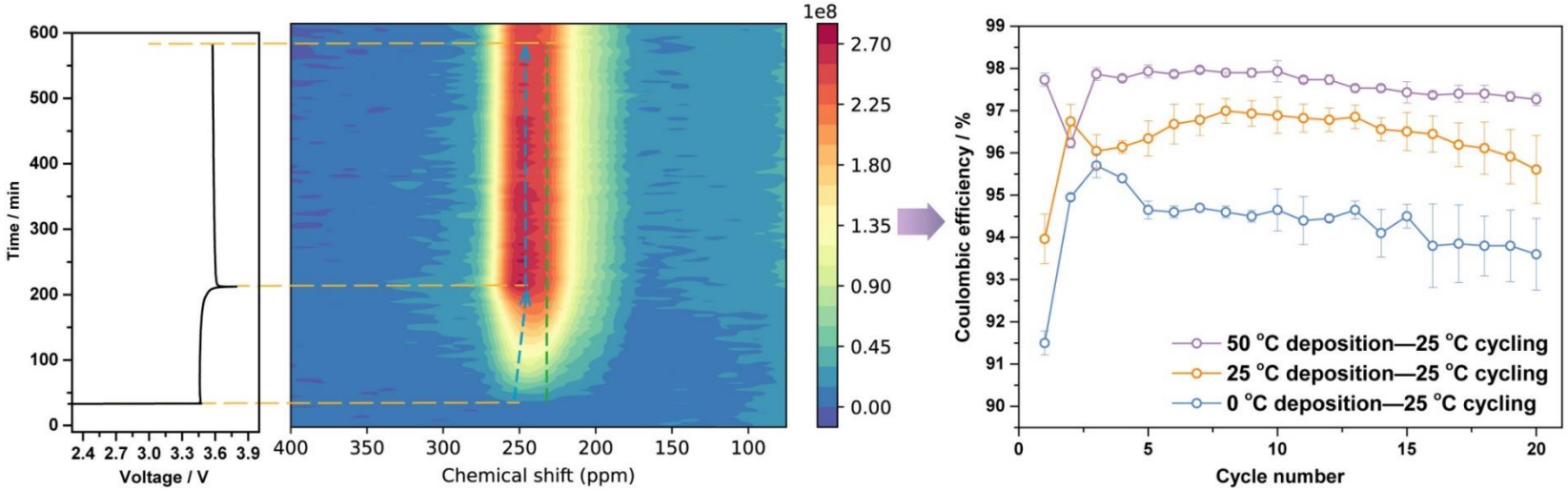
Modification strategies are basically derived from two principles:

(1) Building a thin and stable SEI

(2) Controlling the morphology to achieve highly reversible and compact Li deposition

Take advantage of the favorable dense morphology of Li metal at high temperature

0 °C deposition → 50 °C rest

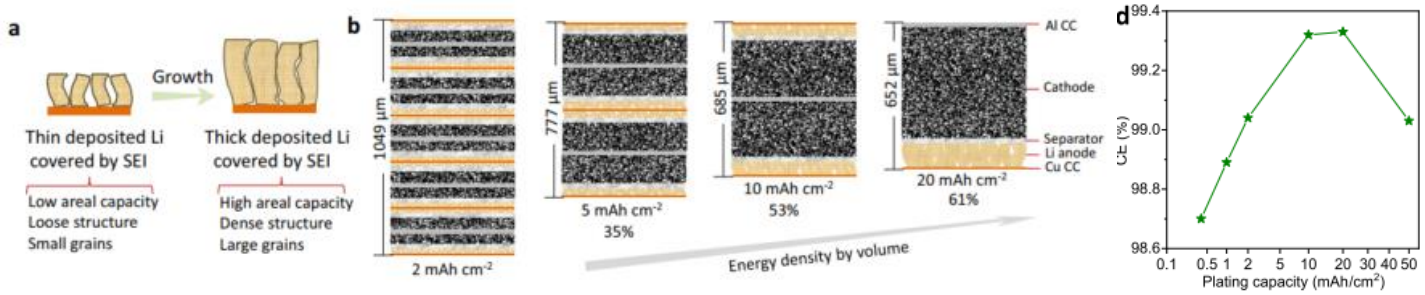


emphasizing the importance of obtaining excellent morphology at the initial deposition

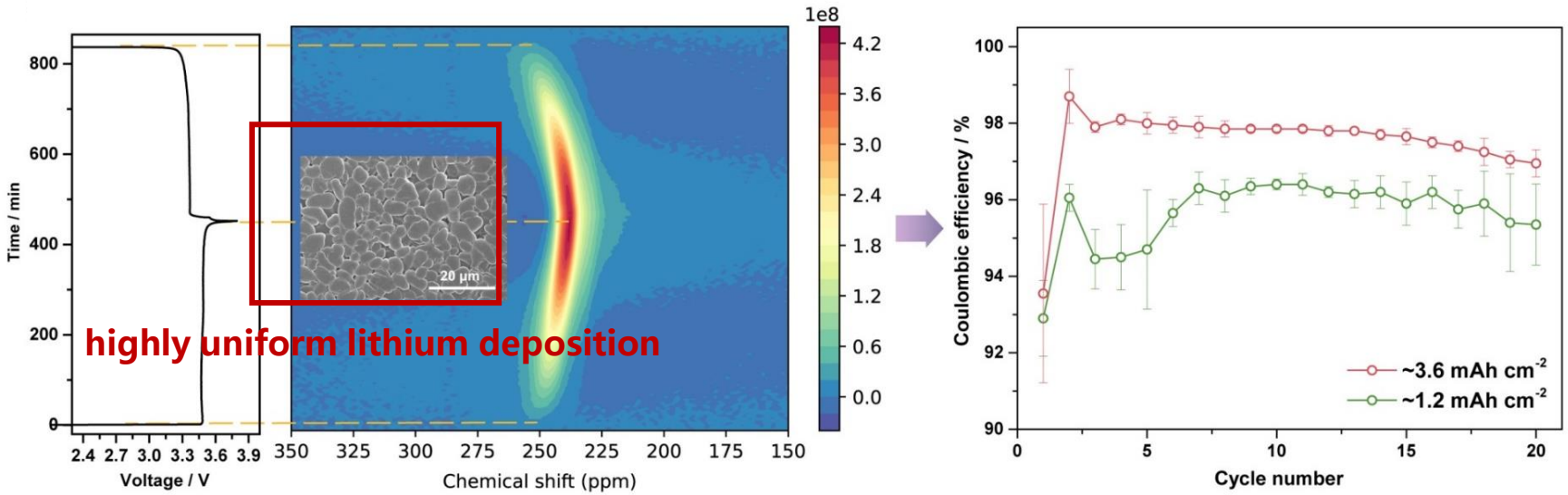
- ✓ **the morphological superiority of 50 °C deposition continues to the subsequent cycles, significantly improving the Coulombic efficiency tested at 25 °C**

Performance-enhancing strategy of Li metal anode

Can dense deposition of Li metal anode be achieved at ambient temperature?



Nat. Commun.,2021, 12, 6034.



The change of chemical shift is more evident under high-capacity lithium deposition, representing a more significant transverse growth of lithium deposits

The $LiFePO_4$||Cu cells exhibit higher Coulombic efficiency

Conclusion

- We employ the operando variable-temperature solid-state NMR technique to systematically study the effect of different temperatures on the evolution of lithium microstructure in the carbonate electrolyte system. The deposition/stripping behavior of lithium metal at 0 °C and 25 °C has a similar evolution pattern, while dense deposited Li metal occurs at 50 °C.
- The phase-filed simulation results illustrate that the dense deposition formed at higher temperature is due to the more uniformly distributed electric field and Li^+ concentration.
- Using MST method, we quantitatively track the evolution of dead Li metal, SEI and LiH at different temperatures, and explain the difference of battery failure mechanism.
- Two strategies were used to achieve more uniform lithium deposition and improve the cycling reversibility of Li metal anodes.

