Build Long-Term Stable High-Energy Lithium Metal Batteries

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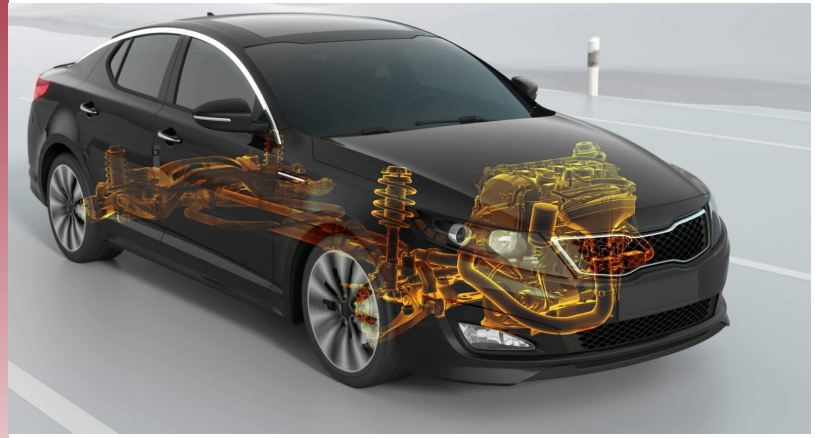
Outline

- Research motivation
- Introduction to ALD and MLD
- ALD sulfide coatings for NMC811
- MLD lithicones for Li metal
- The promising resultant Li||NMC LMBs
- Conclusions
- Acknowledgements

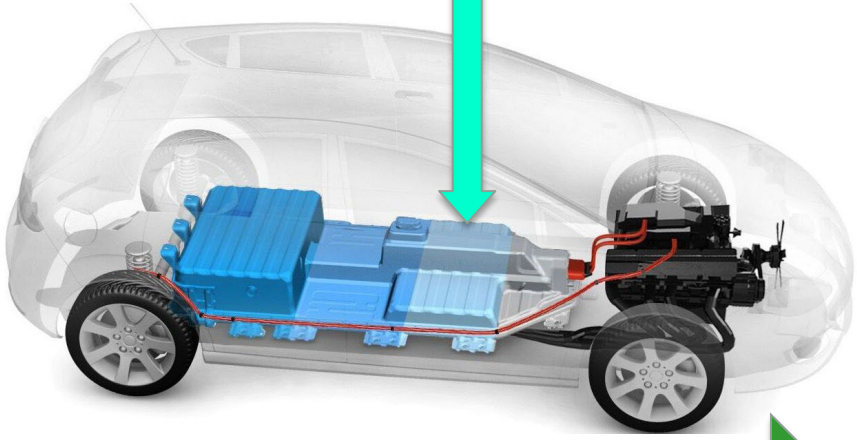
Research motivation

$100/kWh
300 Wh/kg

Conventional vehicles



Electric vehicles



Internal Combustion Engine (ICE) vs. Electric Motor (EM)

Emerging battery systems

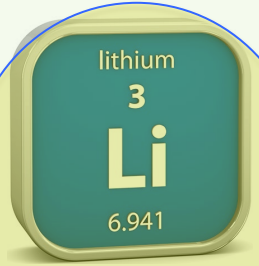
High-energy rechargeable batteries

> 300 Wh/kg; < $100/kWh

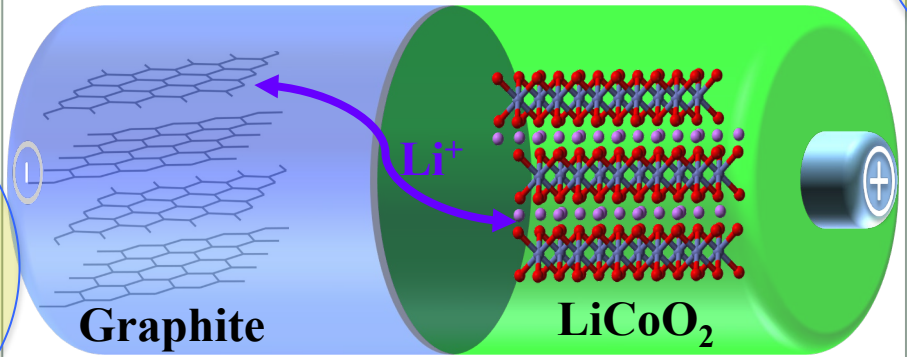
$250/kWh
200 – 250 Wh/kg

Anode

4200 mAh/g



3860 mAh/g

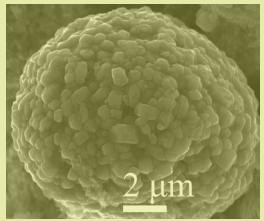


Graphite
372 mAh/g

$LiCoO_2$
140 mAh/g

Cathode

$LiNi_xMn_yCo_zO_2$ (NMCs)



~200 mAh/g

Emerging cathodes:

1675 mAh/g

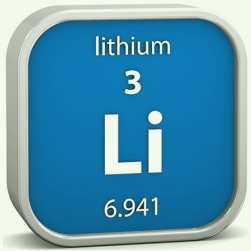
O_2
3350 mAh/g

Lithium metal batteries (LMBs)

High-energy lithium metal batteries (LMBs)

> 300 Wh/kg; < $100/kWh

Anode

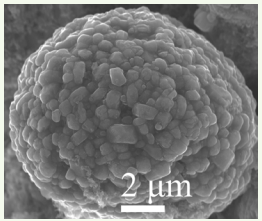


3860 mAh/g

Atomic and Molecular Layer Deposition **(ALD & MLD)**

Cathode

$LiNi_xMn_yCo_zO_2$ (NMCs)

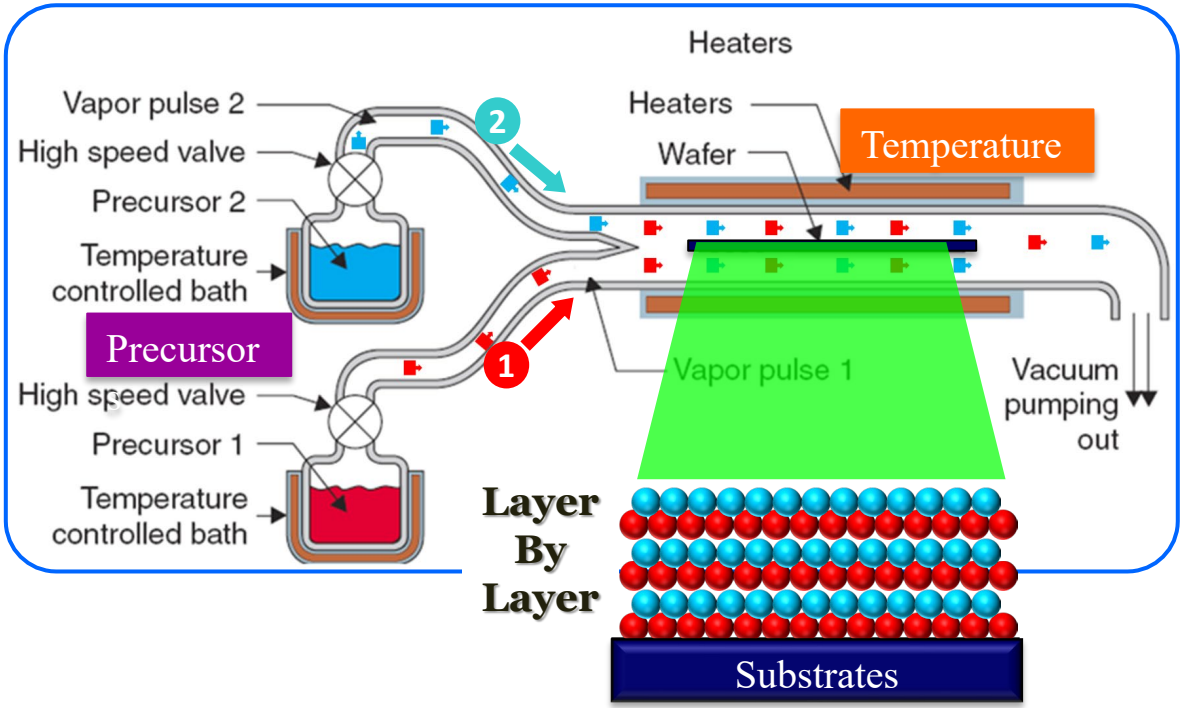


~200 mAh/g

Atomic and Molecular Layer Deposition (ALD & MLD)

Atomic Layer Deposition (ALD)

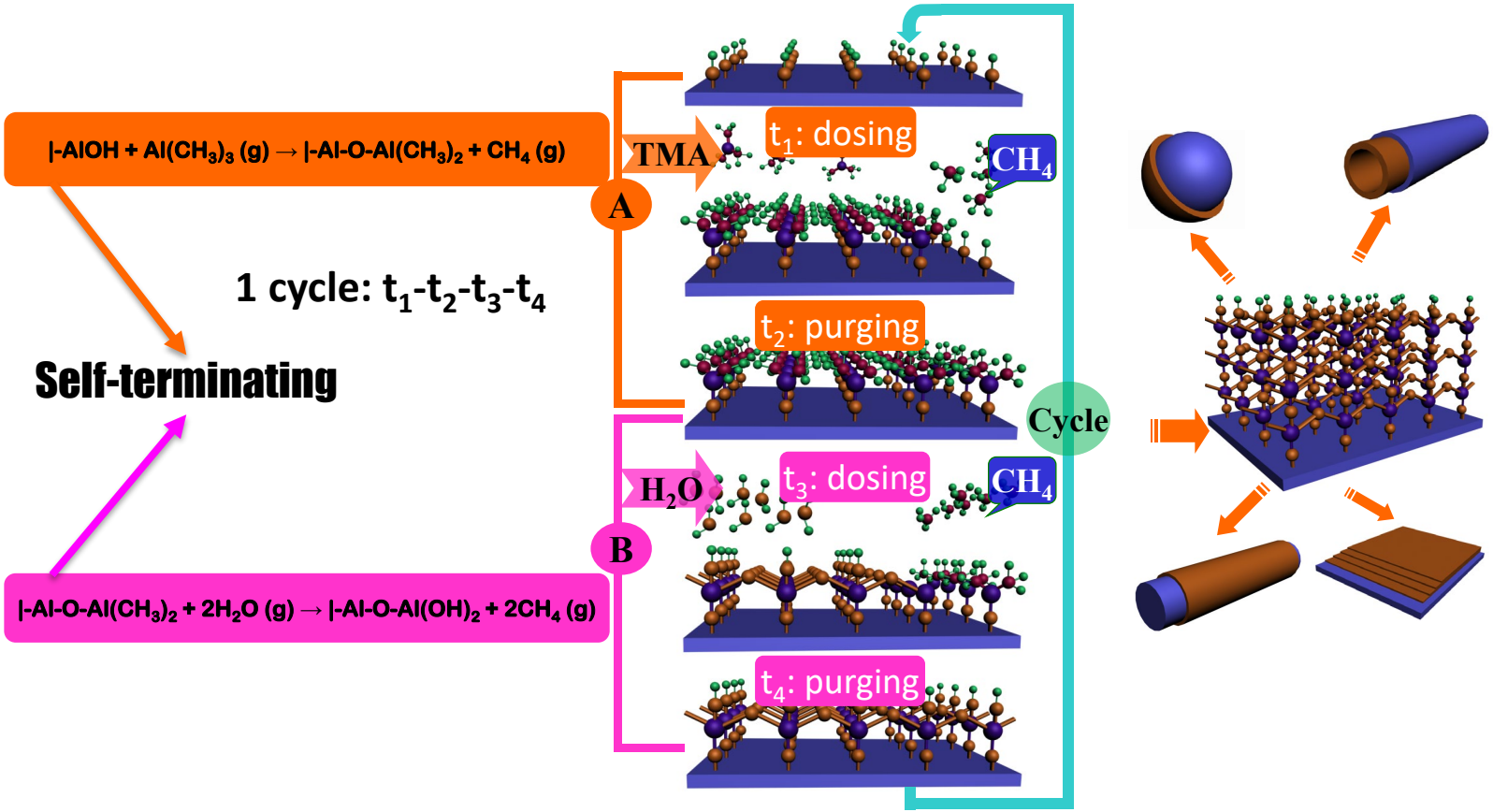
A *surface-controlled* chemical vapor deposition process enabling conformal and uniform films



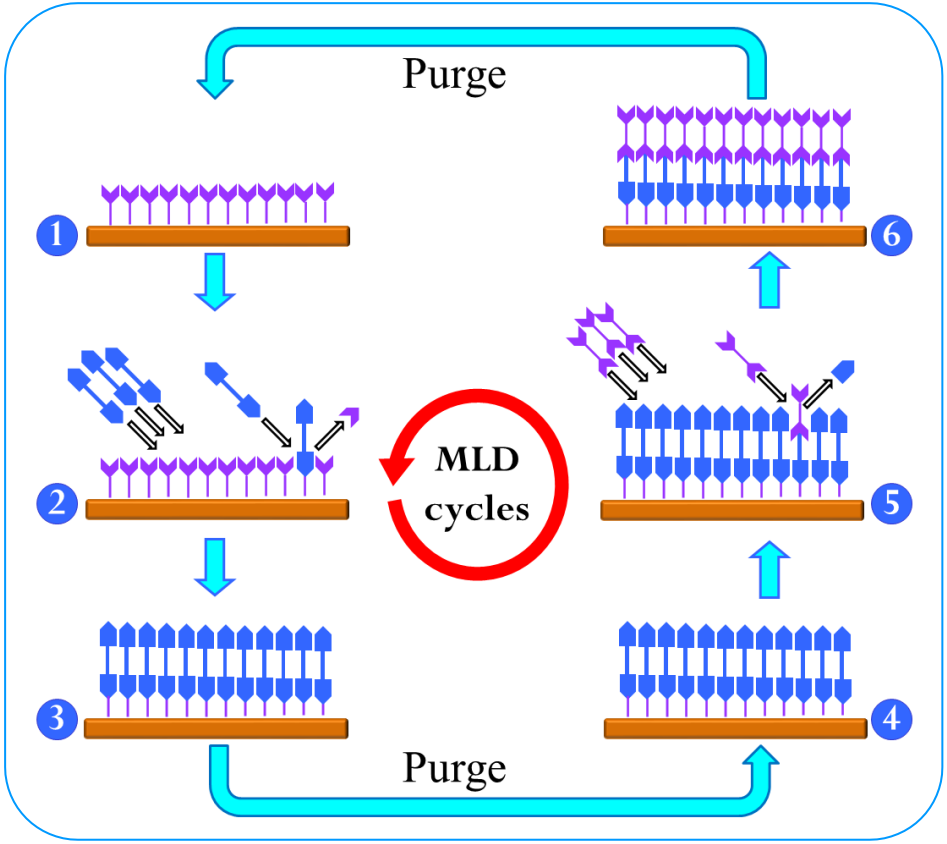
ALD of Al_2O_3

Overall reaction

$2Al(CH_3)_3$ (i.e., TMA)$+ 3H_2O \rightarrow Al_2O_3 + 6CH_4$



ALD/MLD



Pure Organic Materials

- Polyamides
- Polyimides
- Polyazomethines
- Polythioureas
- Polyureas
- Other polymers

Organic-inorganic Hybrid Materials

- Metalcones (alucones, zincones, titanicones, vanadicones, zircones, hafnicones)
- Metal quinolones
- Metal organic frameworks
- Others

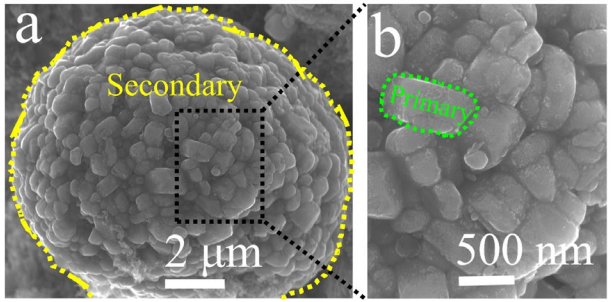
ALD/MLD

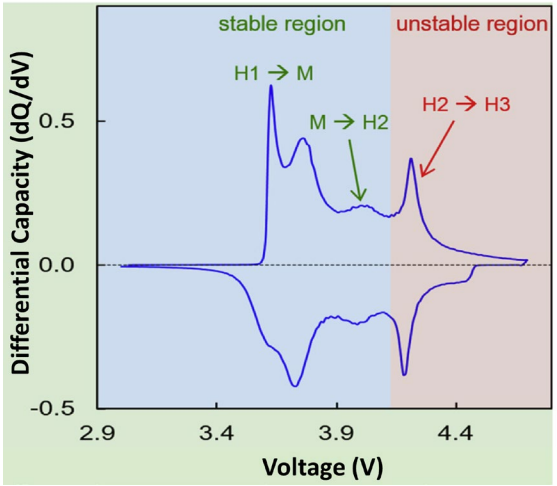
Unique Capabilities of ALD/MLD

- A surface-controlled process proceeded with self-terminating surface reactions
- Atomic/molecular-scale control over materials growth:
  1 -2 Å /cycle for ALD; several Å /cycle for MLD
- Uniform and conformal coating
- Highly tunability in composition and crystallinity
- Low growth temperature: **< 300 °C**
- Nearly any materials, ranging from inorganic to organic materials

ALD Sulfide Coatings for NMC811 Cathodes

Ni-rich NMC cathodes





Cost-effective; higher capacity

NMC111, NMC442, NMC532, NMC622, NMC811

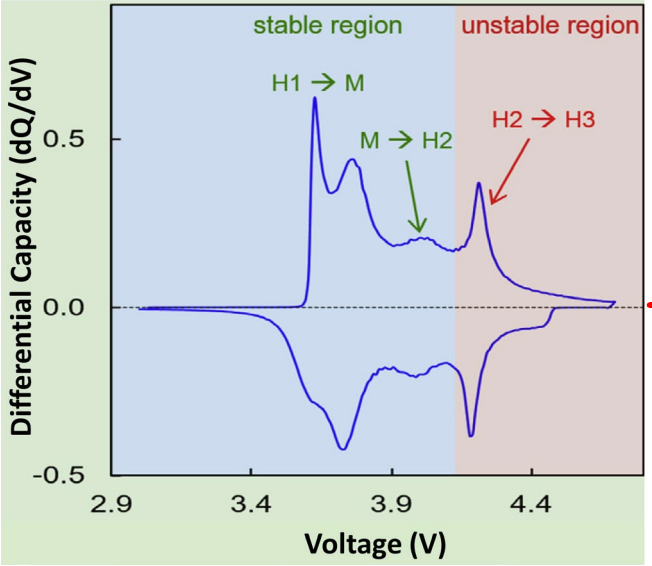
More challenging

Hexagonal (H1) to monoclinic (M) and hexagonal (H2 and H3) phases

The voltage for the H2→H3 phase transition decreases with increased Ni contents, which is ~4.7 V (all voltages in this proposal are against Li/Li^+) for NMCs of $x \leq 0.6$ (e.g., NMC622 and NMC532), but is ~4.3 V for NMC811

Ni-rich NMC cathodes

Issues of NMCs



Hexagonal (H1) to monoclinic (M) and hexagonal (H2 and H3) phases

Oxygen release

Occurred near the onset of H2 → H3

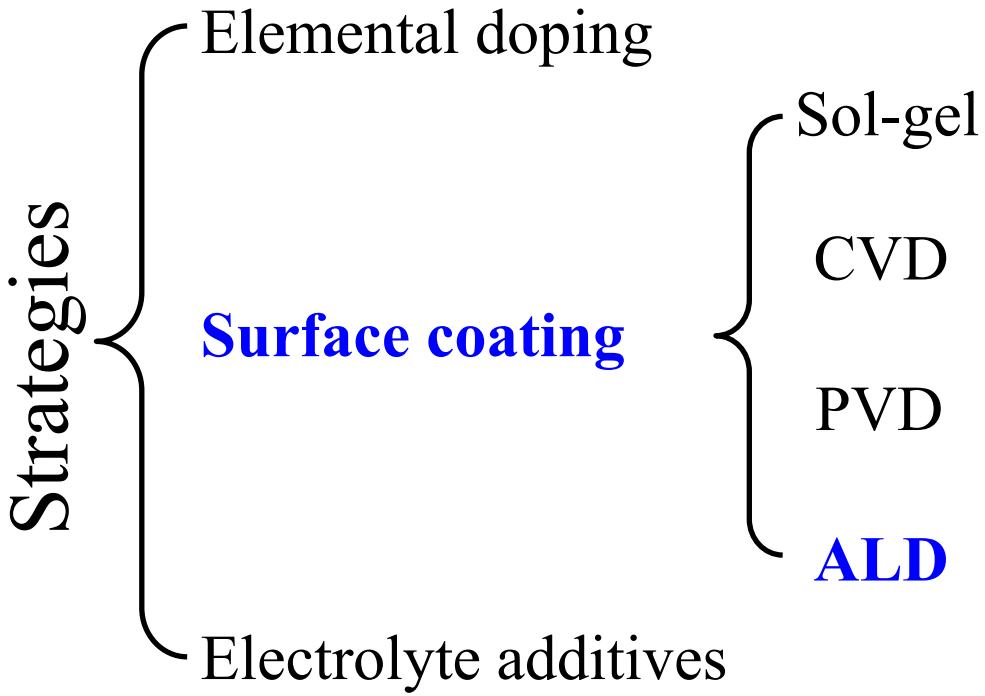
- ❑ **Oxidization of electrolyte solvents** with generation of gases and H_2O
- ❑ **Ni/Li cationic mixing**
- ❑ **Irreversible layered-spinel-rocksalt phase transition**
- ❑ **Transition metal ion dissolution**
- ❑ **Microcracking**

Residual lithium compounds

(RLCs: Li_2CO_3 and LiOH)

- ❑ **Battery gassing**
- ❑ **Electrode structural degradation**

Atomic layer deposition (ALD) for better batteries



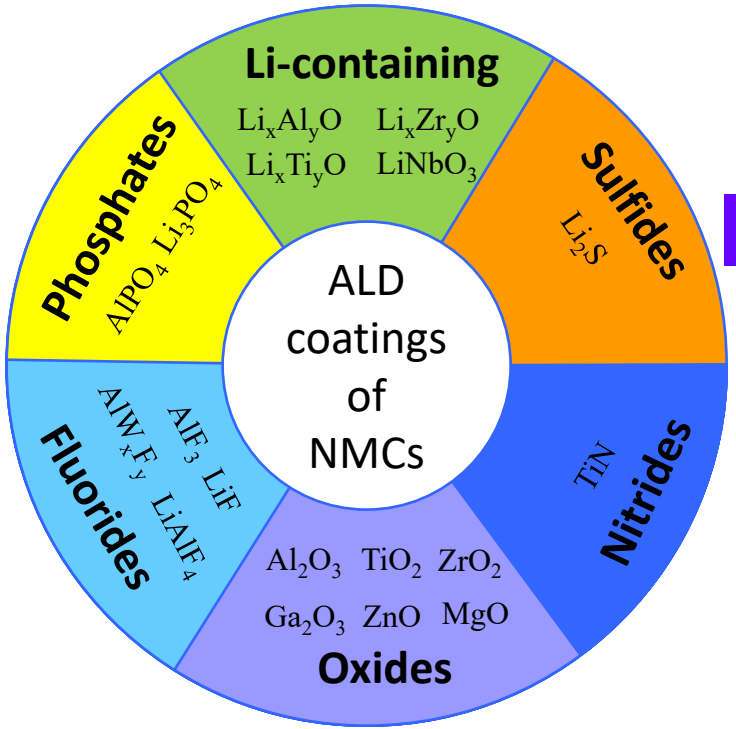
Atomic layer deposition (ALD) for better batteries

ALD can coat either electrode materials or prefabricated electrodes.

ALD is to date *the only technique* enabling coatings over electrodes directly.

ALD coatings of NMCs

Rare Met. 2023, 42, 2121 – 2156.



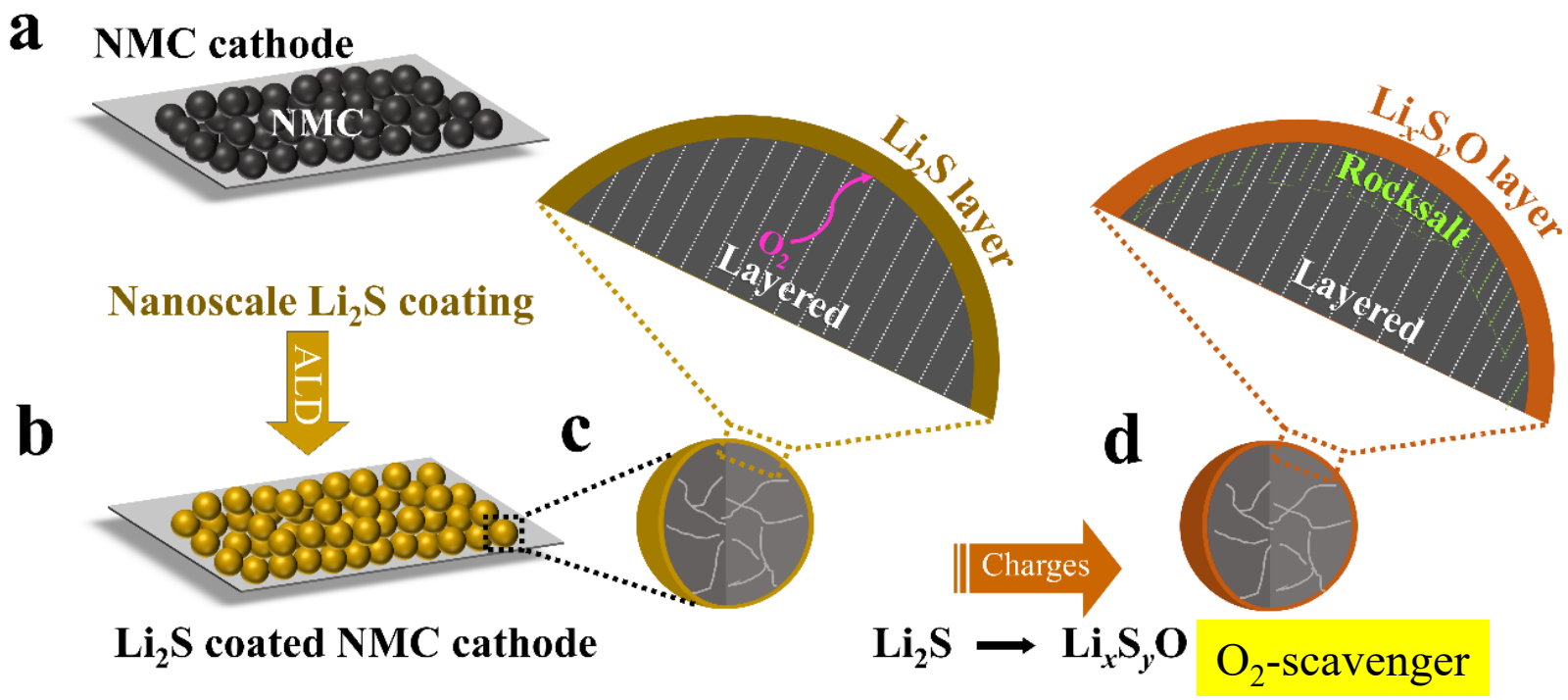
Journal of Energy Chemistry, 2022, 69, 531 – 540.

The first study investigating sulfides as surface coatings via ALD, in which Li_2S showed excellent protection over NMC811.

Li_2S on NMC811 electrodes

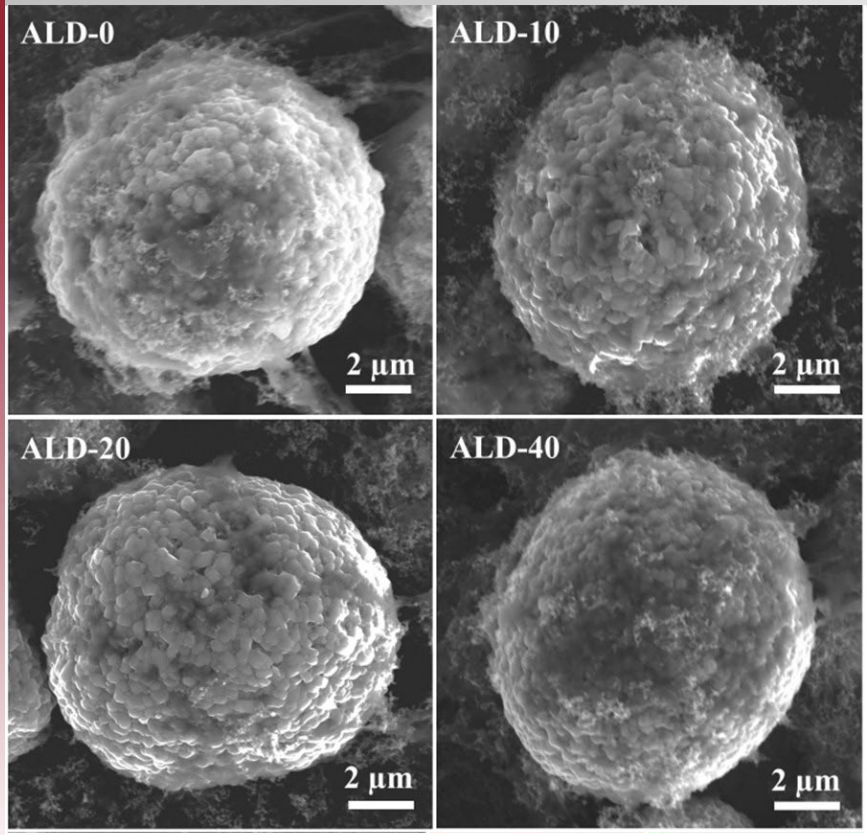
J. Energy Chem. 2022, 69, 531 – 540

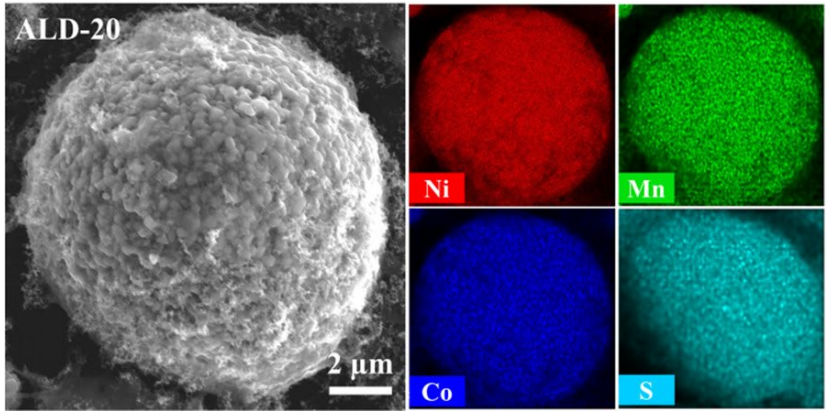
We **for the first time** revealed that sulfides are an unexplored class of coating materials having some unique benefits!



Effects of ALD Li_2S on NMC811 electrodes

J. Energy Chem. 2022, 69, 531 – 540





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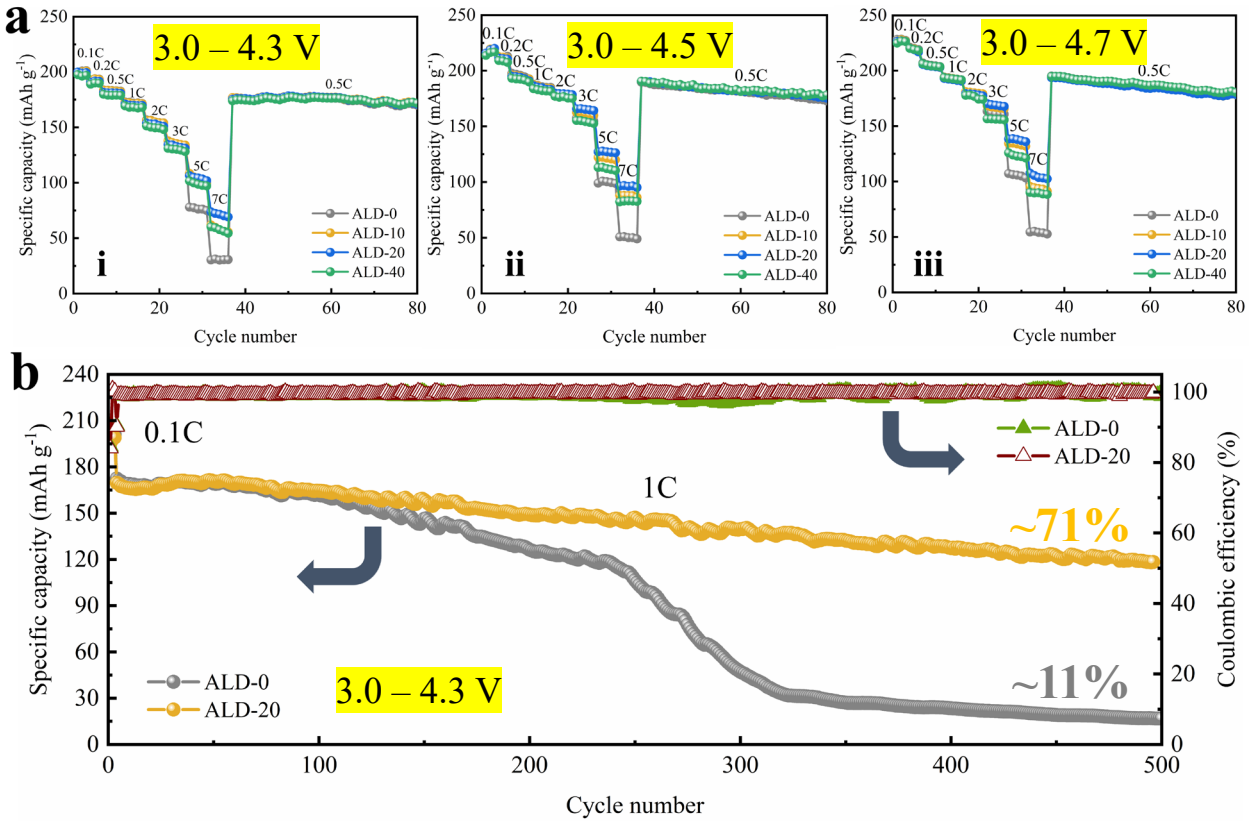
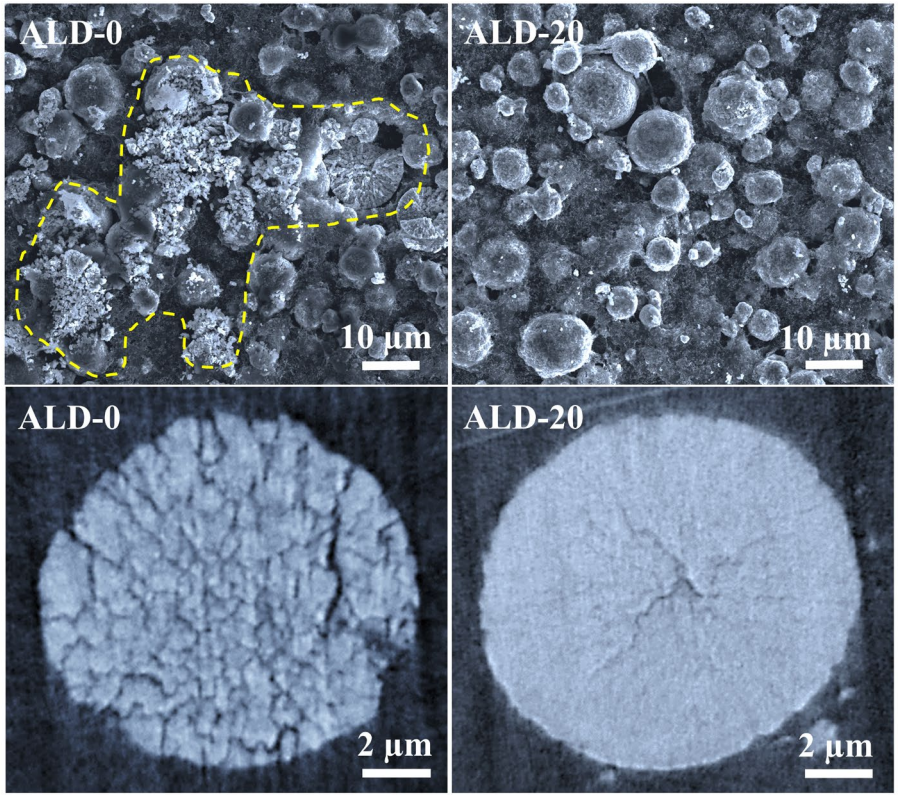


Effects of ALD Li_2S on NMC811

J. Energy Chem. 2022, 69, 531 – 540

NMC811 suffer from serious cracking during cycling

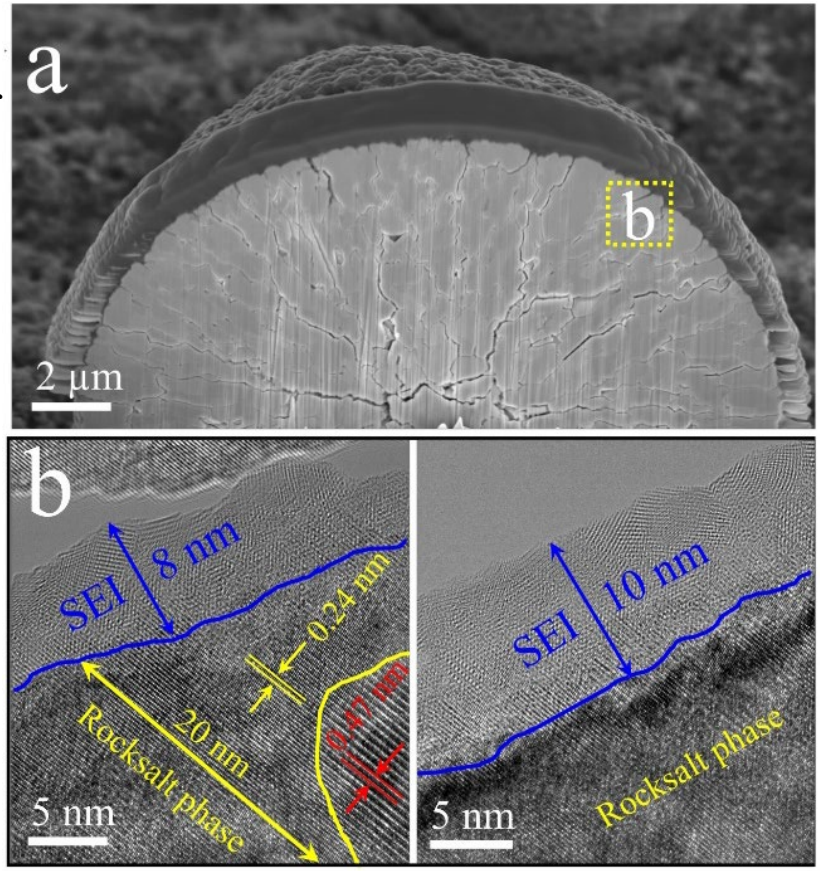


ALD Li_2S coating well protected NMC811 from cracking

Effects of ALD Li_2S on NMC811 electrodes

J. Energy Chem. 2022, 69, 531 – 540

Bare NMC811 after 500 ch/disch cycles

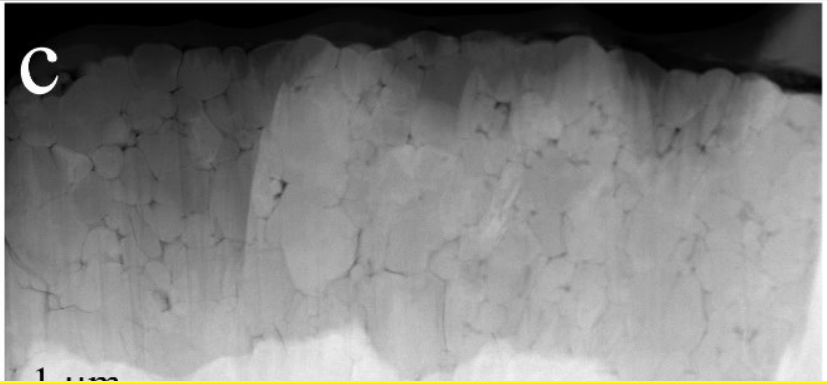


- Large cracks
- Thick CEI
- Evident formation of NiO-like rocksalt phase

Effects of ALD Li_2S on NMC811 electrodes

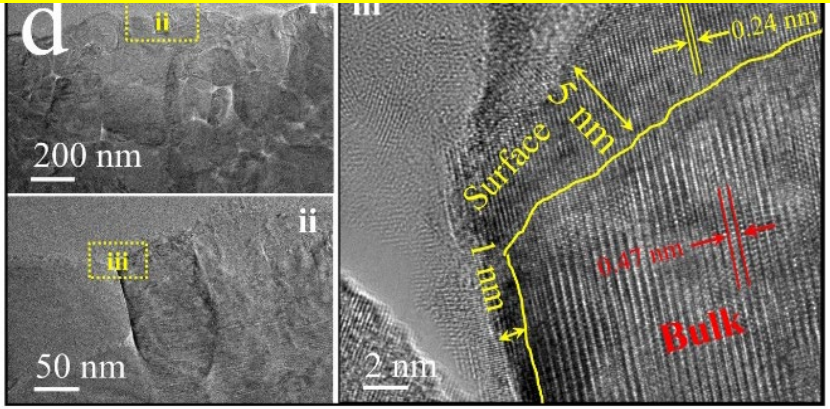
J. Energy Chem. 2022, 69, 531 – 540

Li_2S-coated NMC811 after 500 ch/disch cycles



- Unnoticeable cracks

ALD Li_2S coating protected NMC cathodes from structural degradation.



- Thin CEI
- Thin NiO-like rocksalt phase

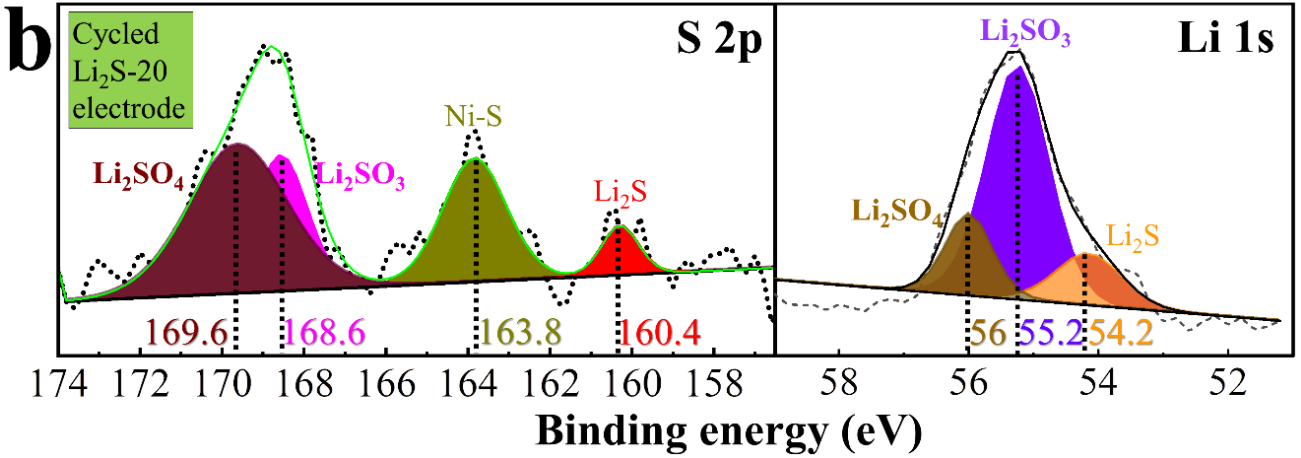
Transformation of ALD Li_2S electrodes

J. Energy Chem. 2022, 69, 531 – 540

ALD Li_2S coating protected electrolytes from oxidation and any further side reactions:

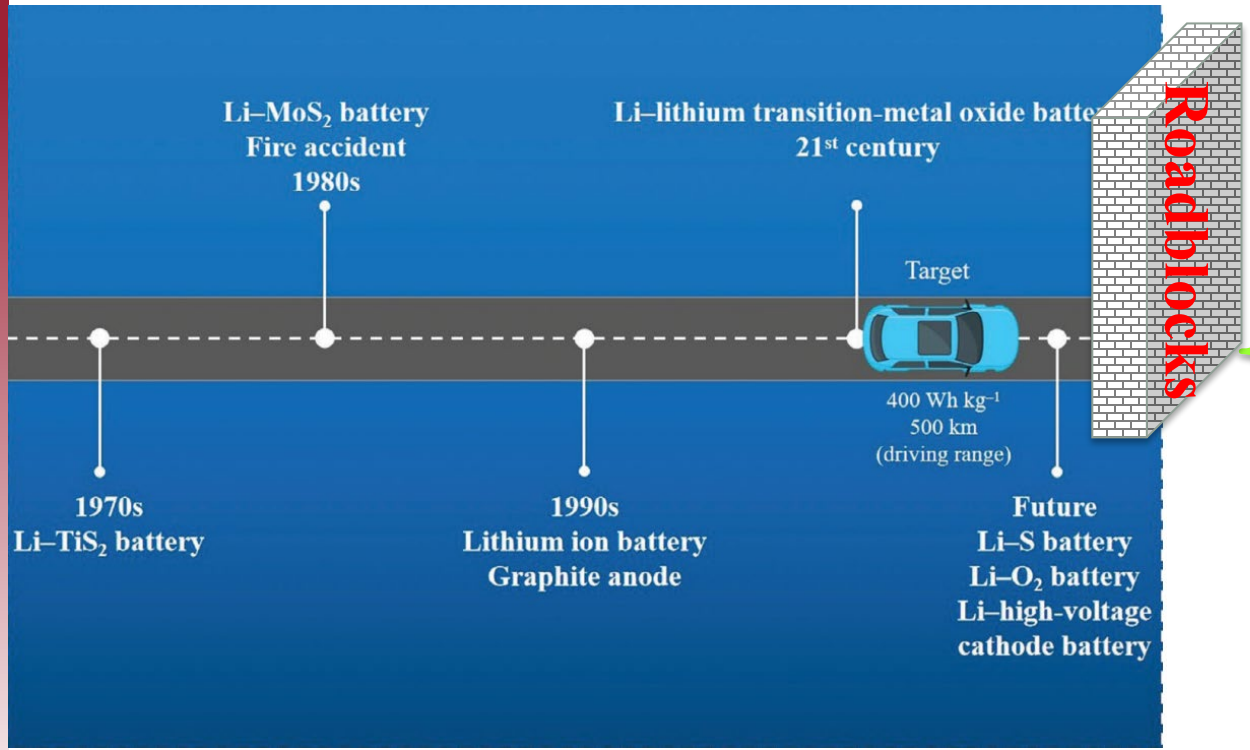
$2Li_2S + 3O_2 \rightarrow 2Li_2SO_3$ (lithium sulfite)

$2Li_2SO_3 + O_2 \rightarrow 2Li_2SO_4$ (lithium sulfate)



MLD Lithicone Coatings for Li Metal Anodes

Challenges facing lithium metal anodes



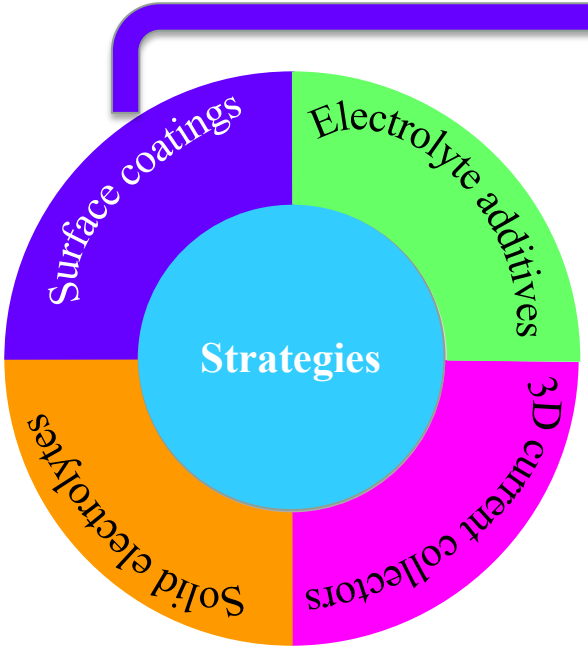
Continuous formation of SEI

Self-accelerated

Lithium dendrites

Adv. Sci. 2021, 8, 2101111

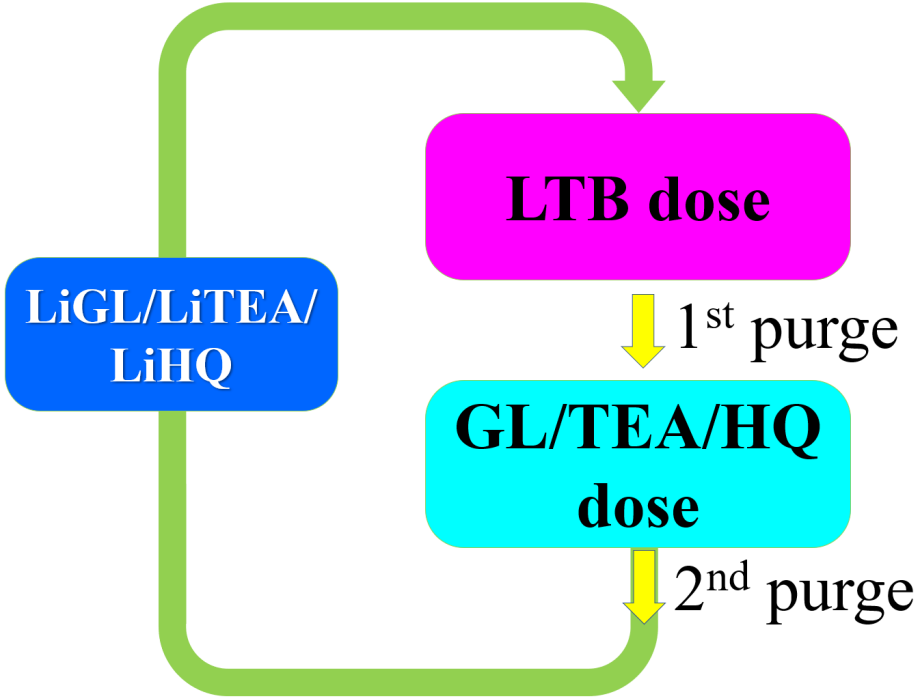
A variety of strategies developed



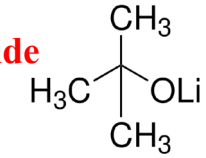
- Physical vapor deposition (PVD)
- Wet chemistry
- Atomic layer deposition (ALD)
- Molecular layer deposition (MLD)

MLD processes for lithicones

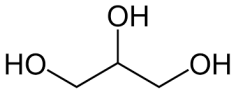
Lithicones: are polymeric lithium alkoxides with carbon-containing backbones, i.e., -Li-O-R-O-Li-.



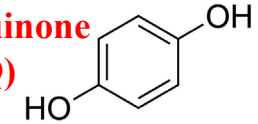
Lithium tert-butoxide (LTB)



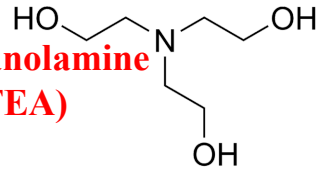
Glycerol (GL)



Hydroquinone (HQ)

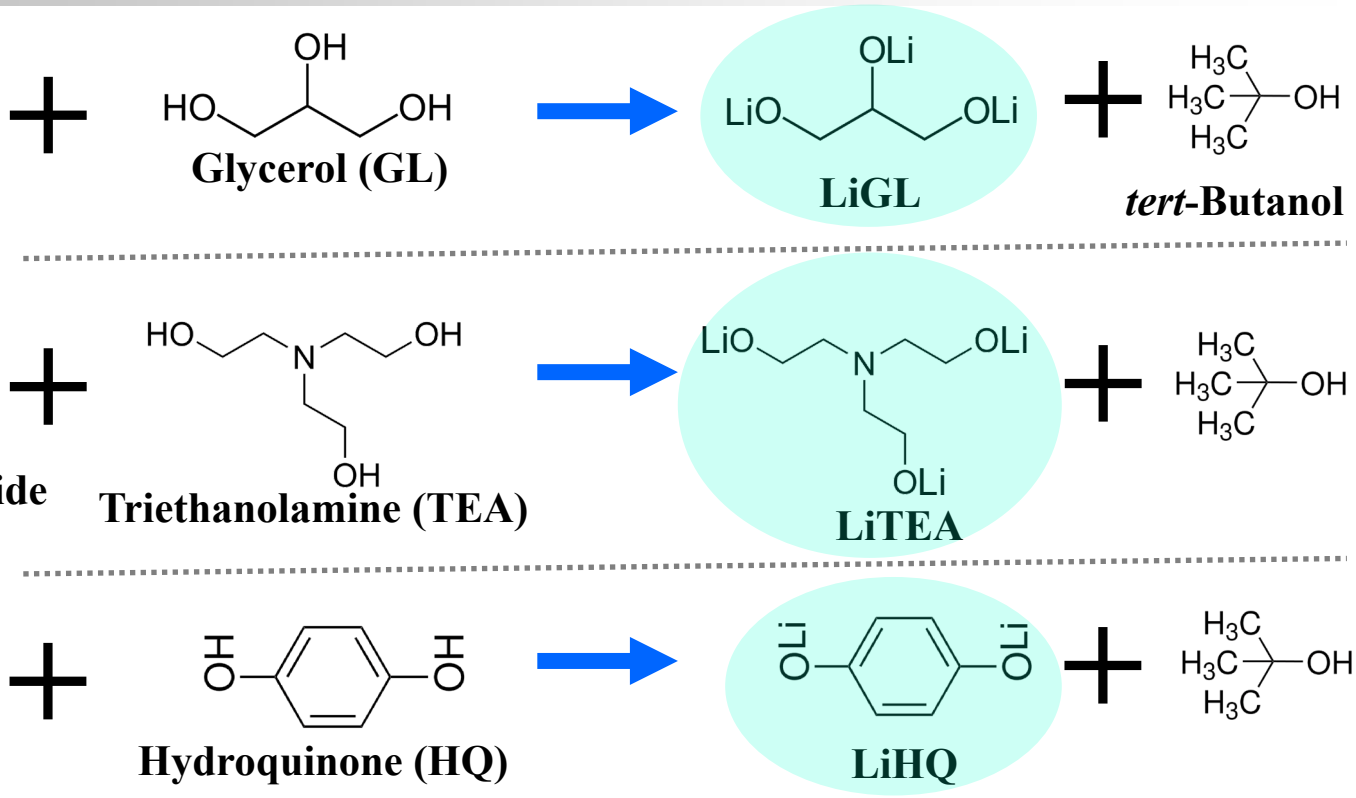


Triethanolamine (TEA)



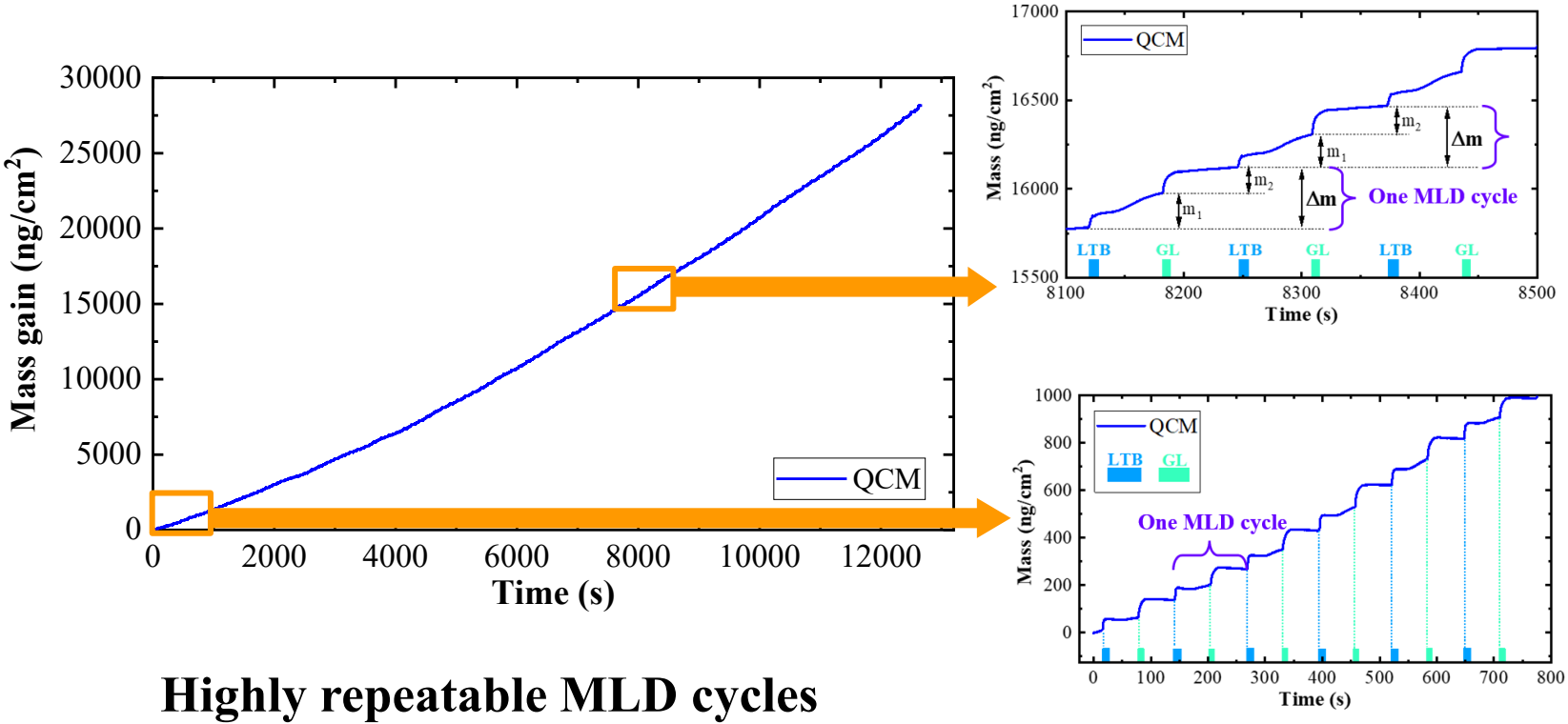
MLD of lithicones

-Li-O-R-O-Li-



QCM measurements of LiGL

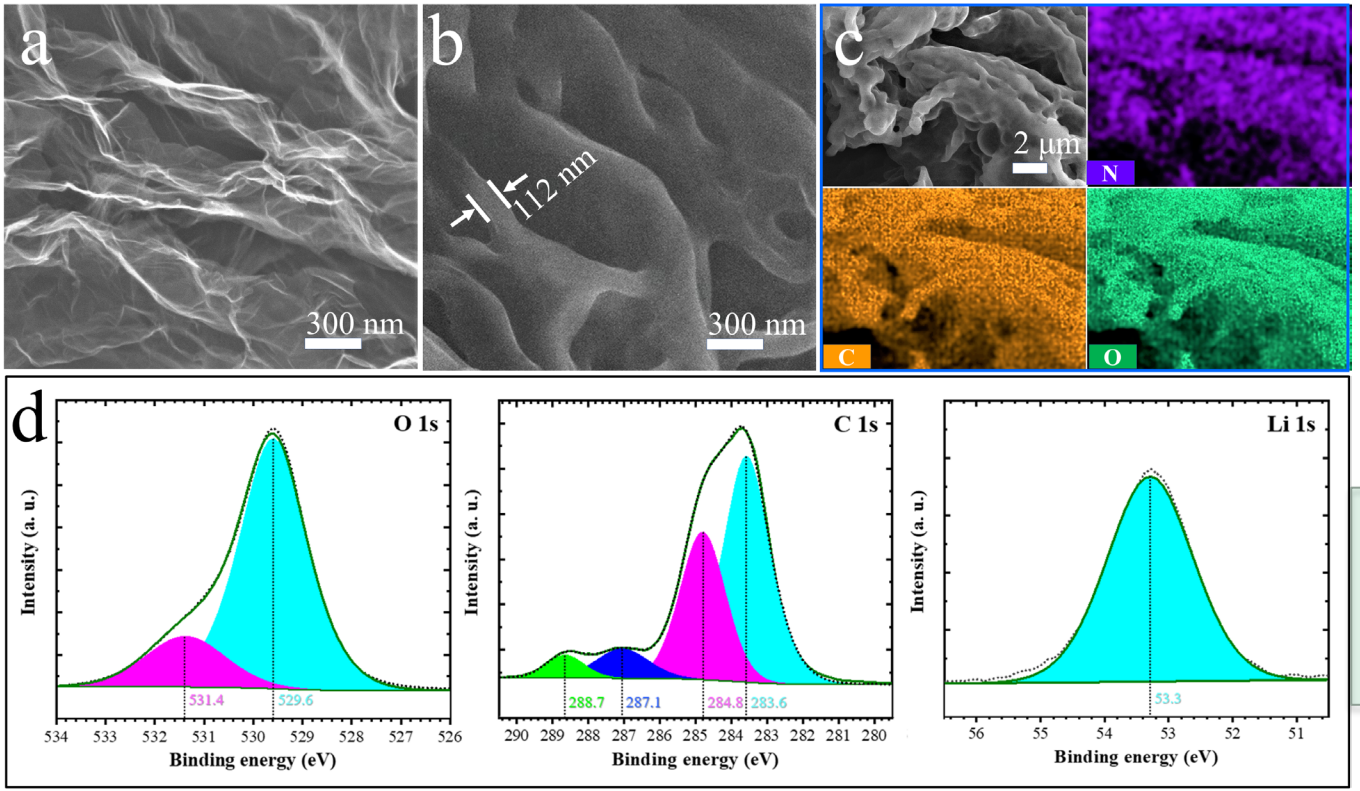
Energy Mater. Advances 2021, 9786201



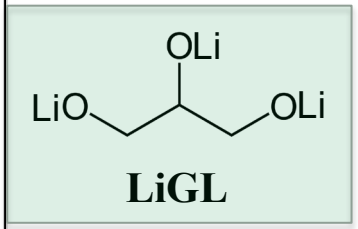
Highly repeatable MLD cycles

SEM and XPS analyses of LiGL

Energy Mater. Advances 2021, 9786201

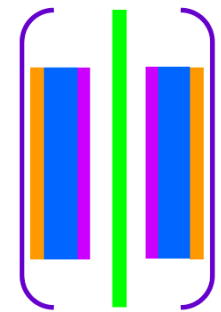


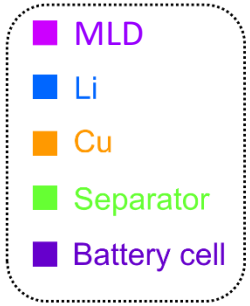
GPC:
2.7 nm/cycle

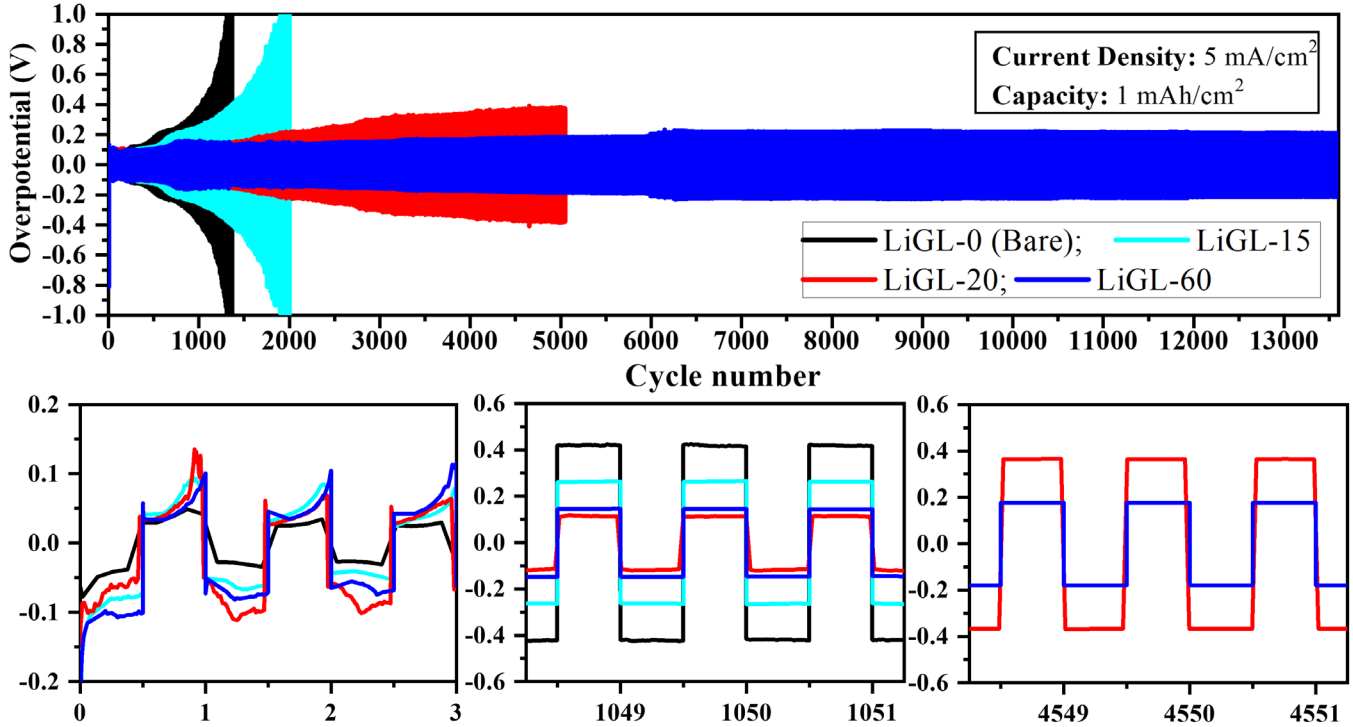


Effects of LiGL on Li metal anode

Energy Mater. Advances 2021, 9786201







Effects of LiGL on Li metal anode

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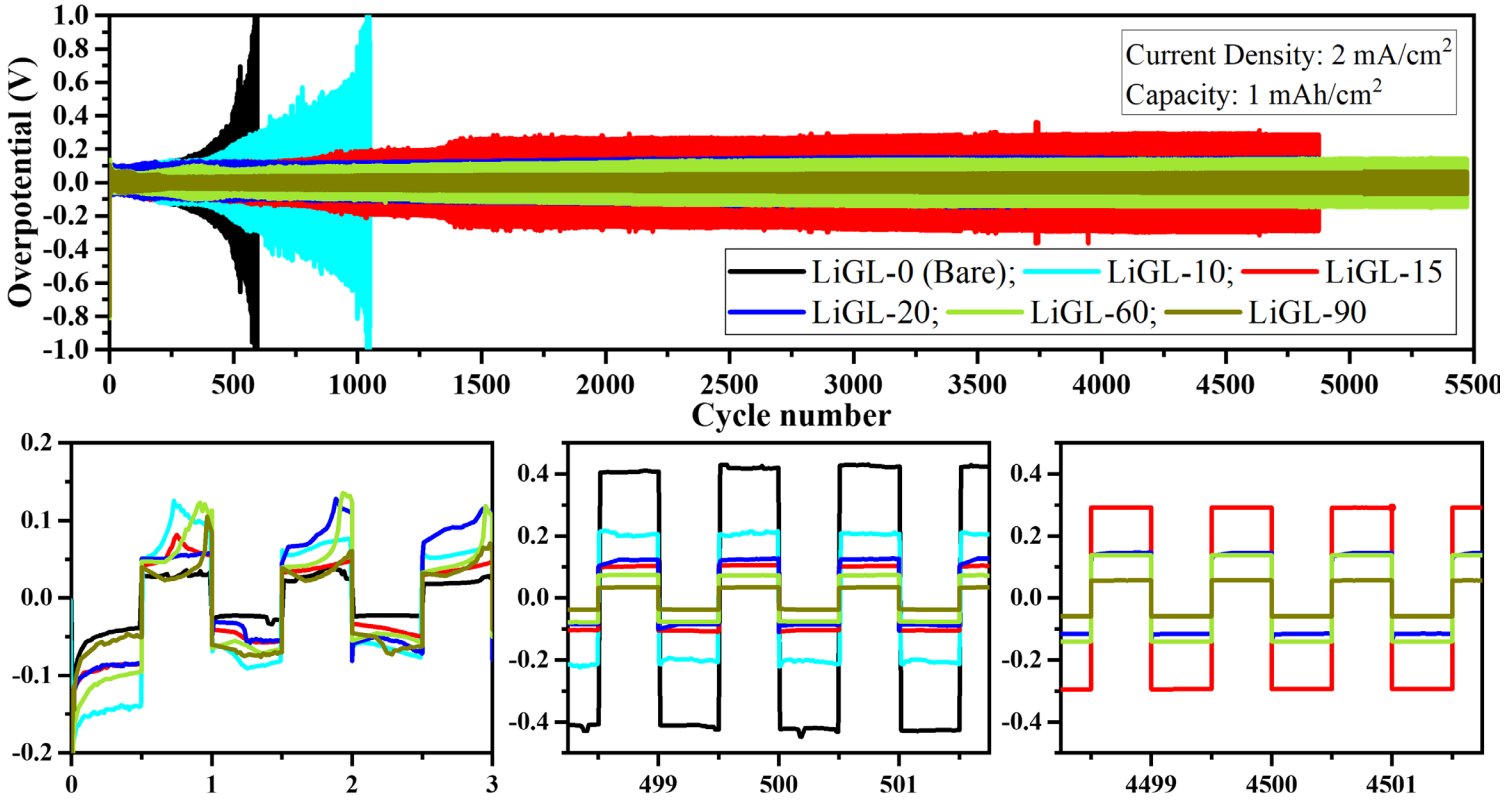
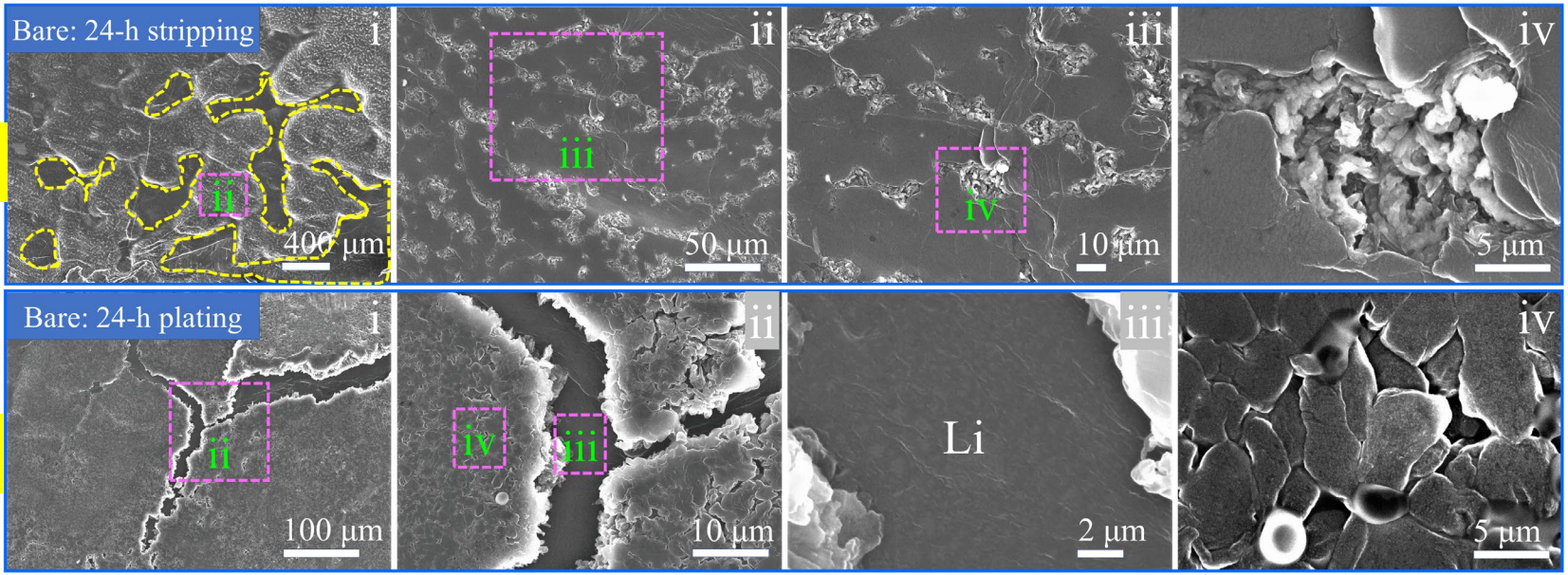


SEM observations of cycled Li||Li cells

Energy Mater. Advances 2021, 9786201

Stripping

Plating



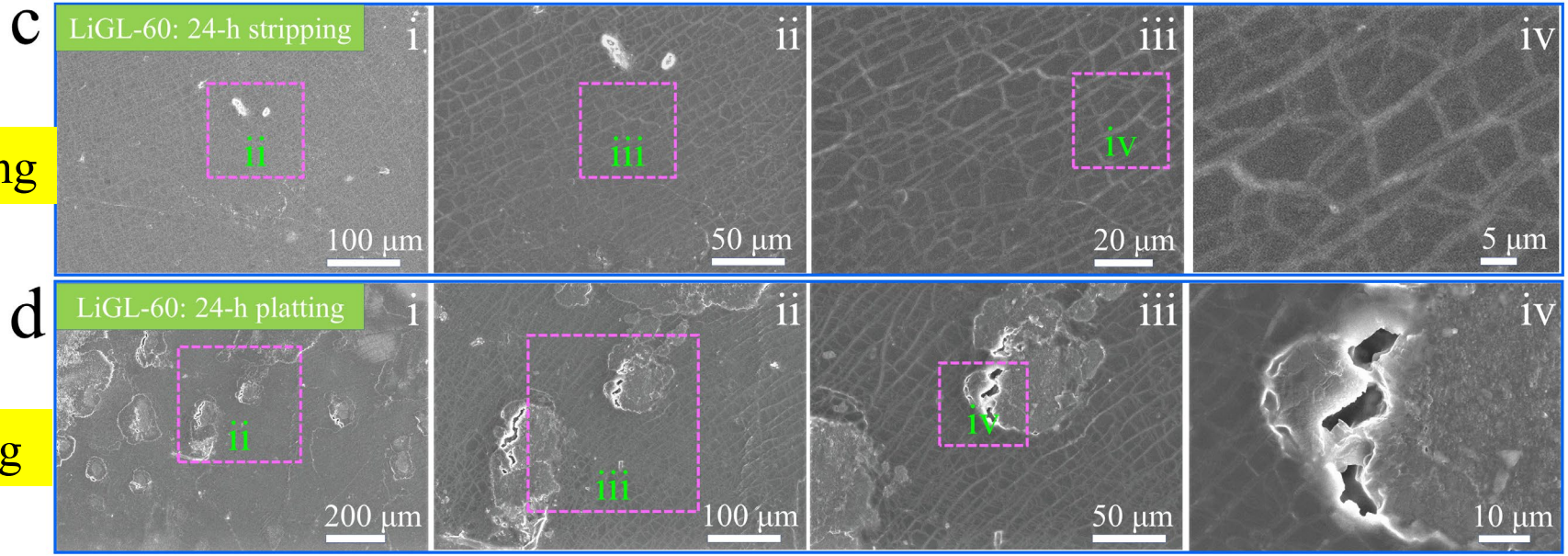
2 mA/cm^2, 48 mAh/cm^2

SEM observations of cycled Li||Li cells

Energy Mater. Advances 2021, 9786201

Stripping

Plating



2 mA/cm^2, 48 mAh/cm^2

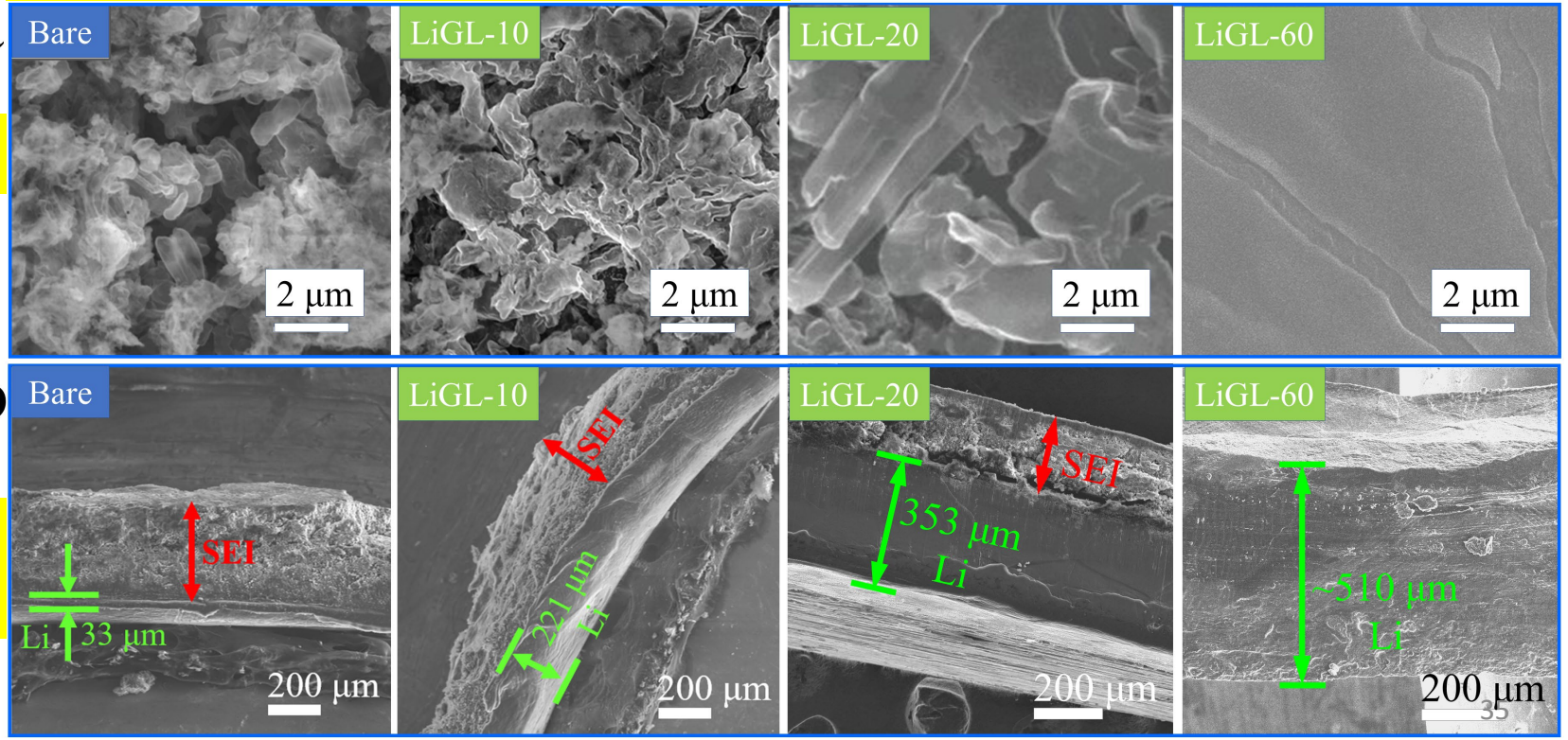
SEM observations of cycled Li||Li cells

Energy Mater. Advances 2021, 9786201

After 700 Li-stripping/plating cycles

Surface

Cross-section



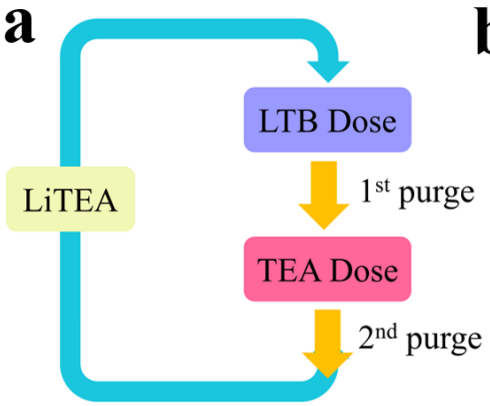
SEM observations of cycled Li||Li cells

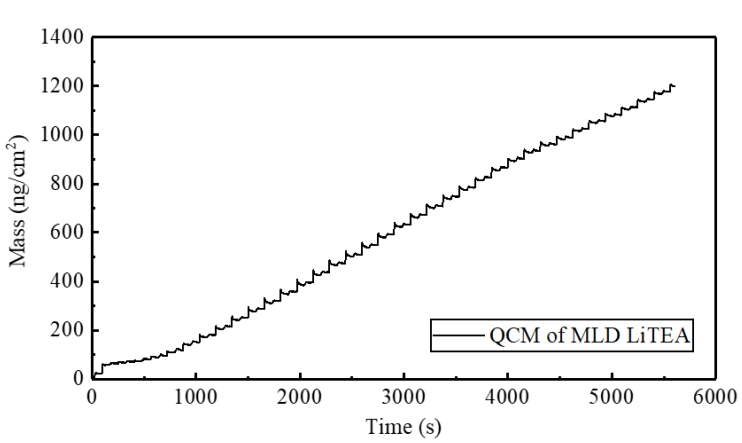
Energy Mater. Advances 2021, 9786201

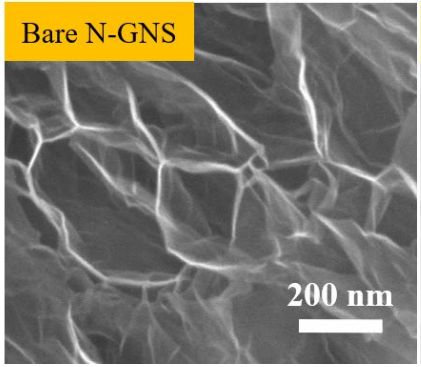
LiGL MLD coating could well protect Li metal from SEI formation and Li dendrite growth.

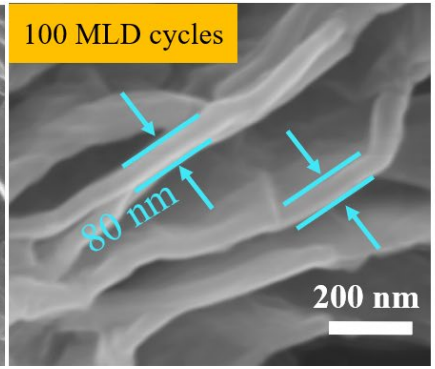
2. MLD lithicones – LiTEA on Li anode

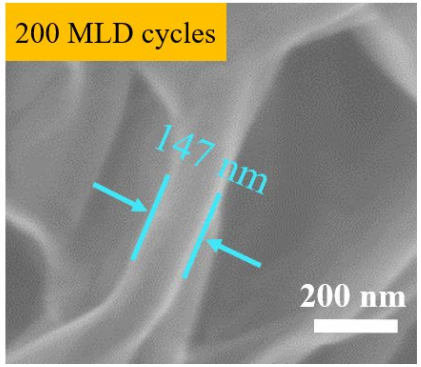
Chemical Engineering Journal 2023, 475, 146156







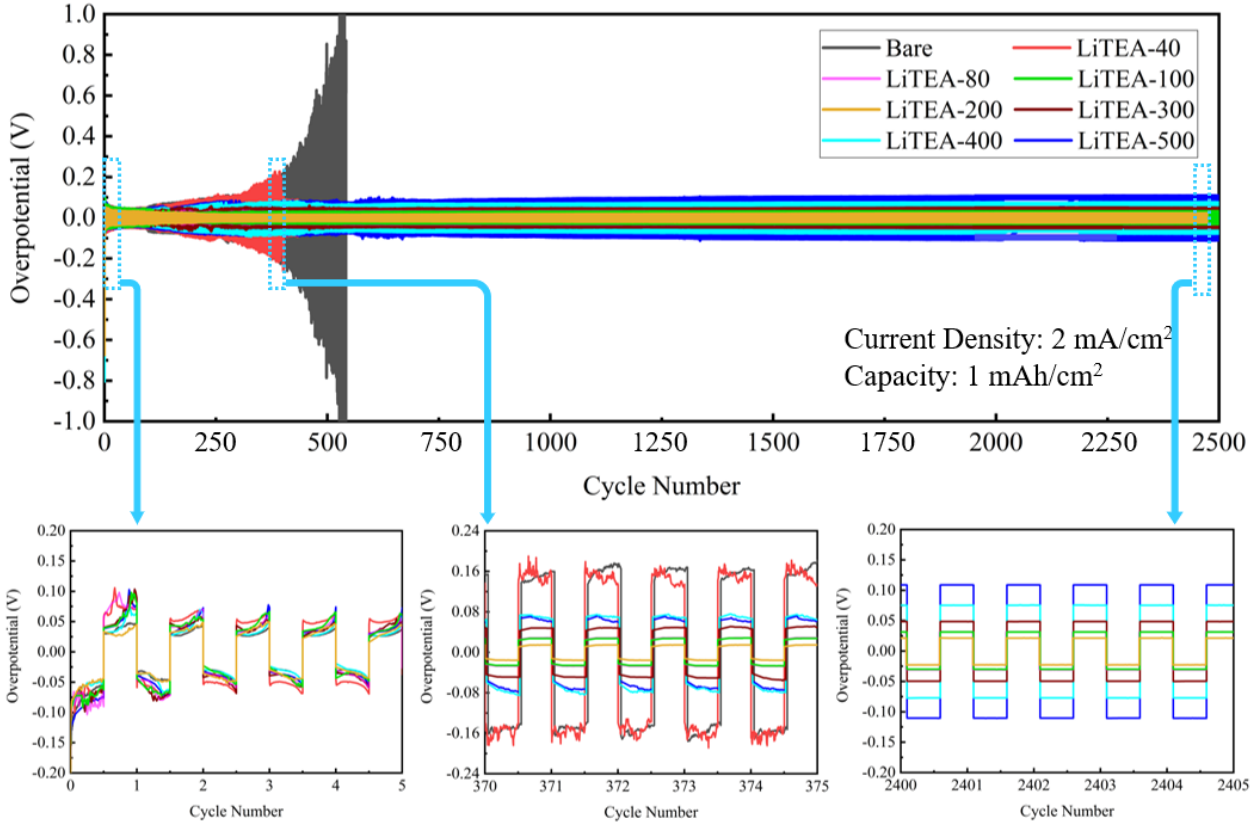




GPC:
~3.6 Å /cycle

LiTEA coating improved cell performance

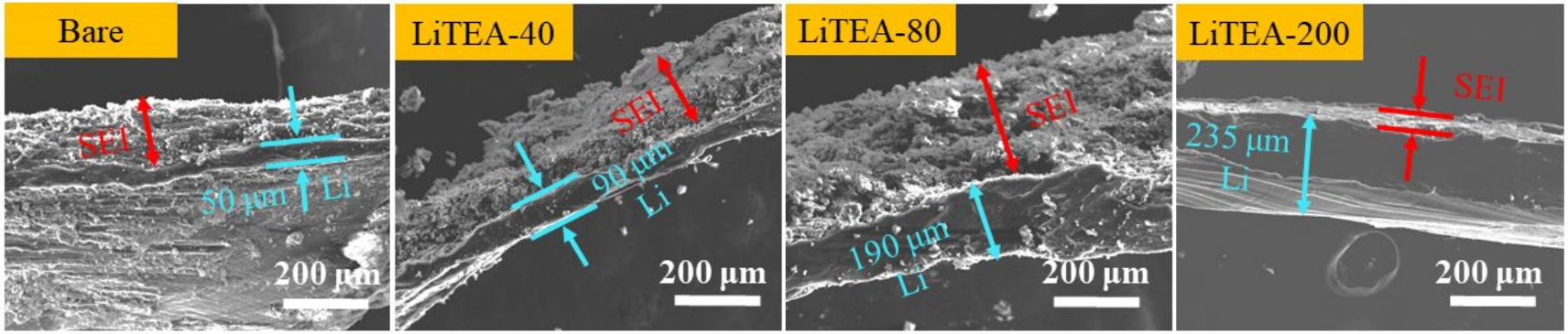
Chemical Engineering Journal 2023, 475, 146156



LiTEA-200 is optimal.
~72 nm

LiTEA protection Li anodes from corrosion

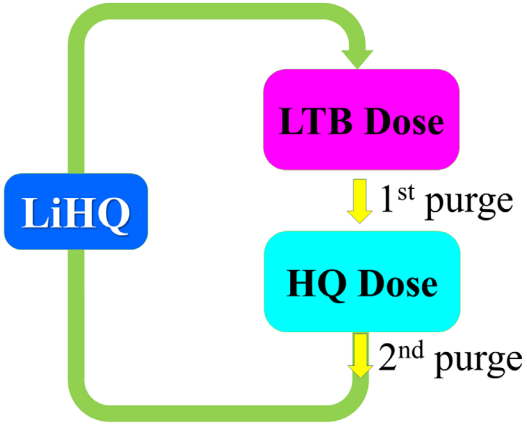
Chemical Engineering Journal 2023, 475, 146156

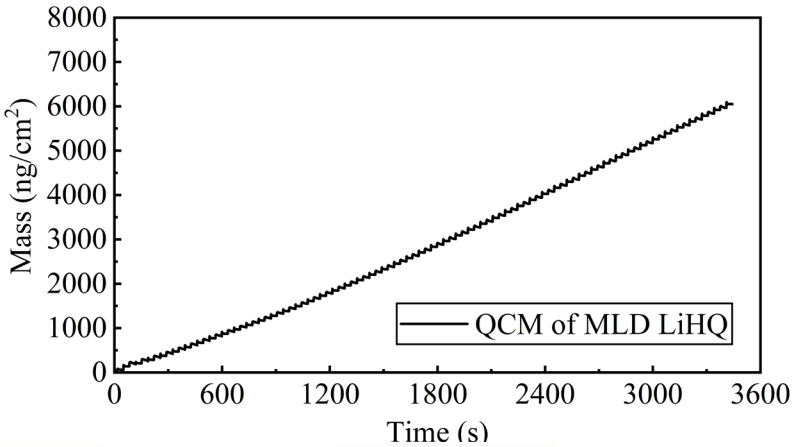


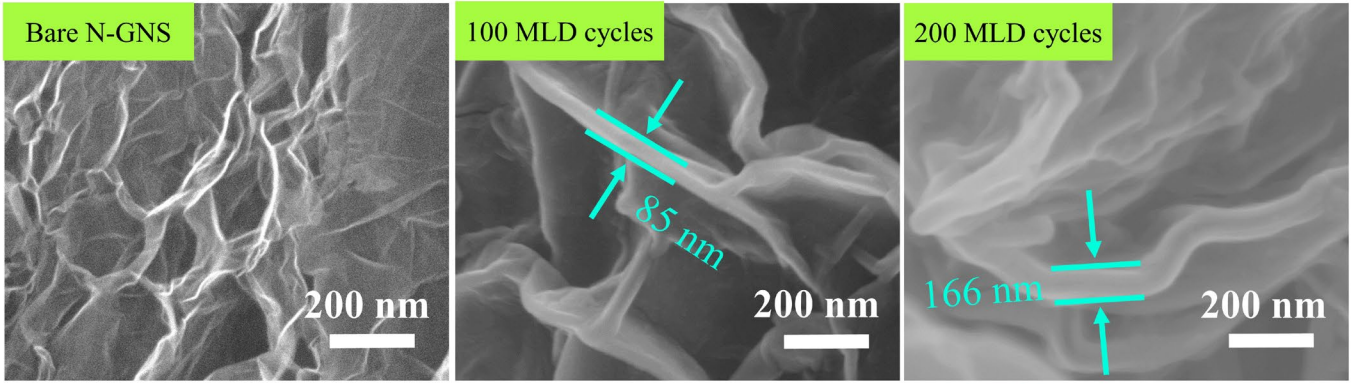
After 500 Li-stripping/plating cycles at 2 mA/cm^2 and 1 mAh/cm^2.

3. MLD lithicones – LiHQ on Li anode

Nano Energy 2024, 128, 109840



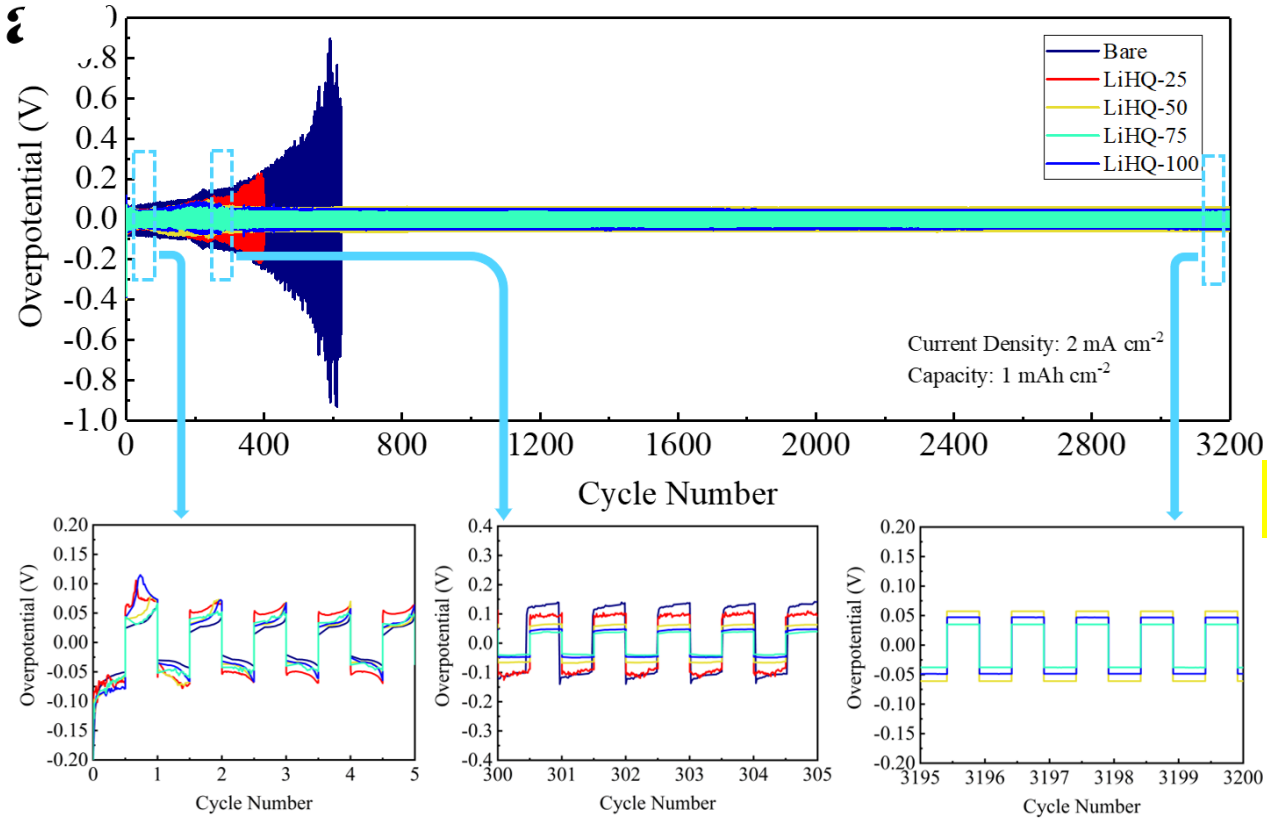




GPC:
~4.0 Å /cycle

Effects of LiHQ on Li metal anode

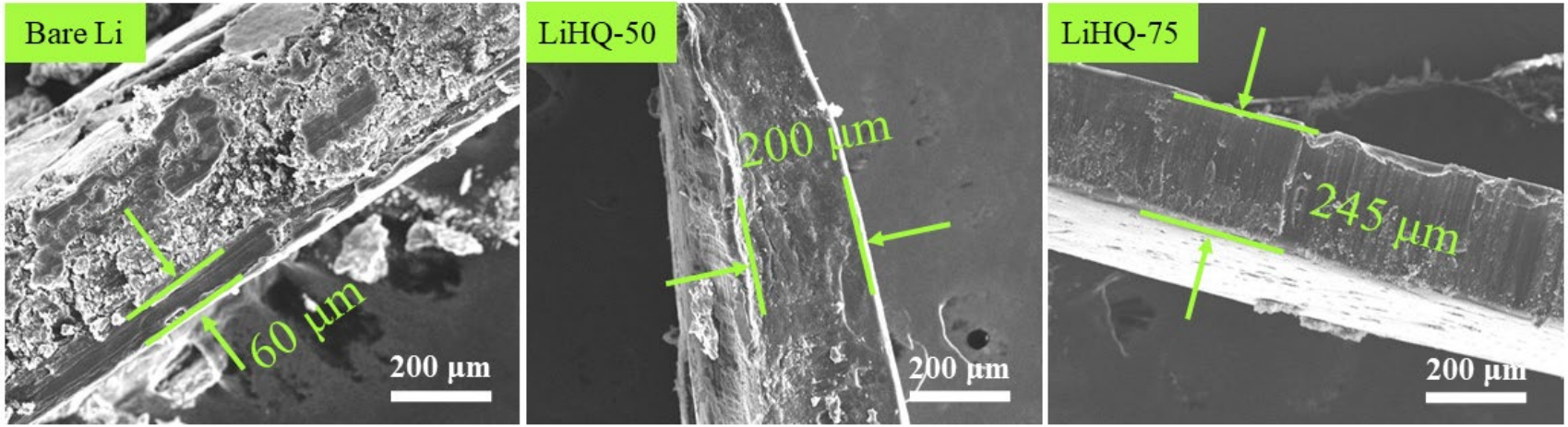
Nano Energy 2024, 128, 109840



LiHQ-75 is optimal

Effects of LiHQ on Li metal anode

Nano Energy 2024, 128, 109840

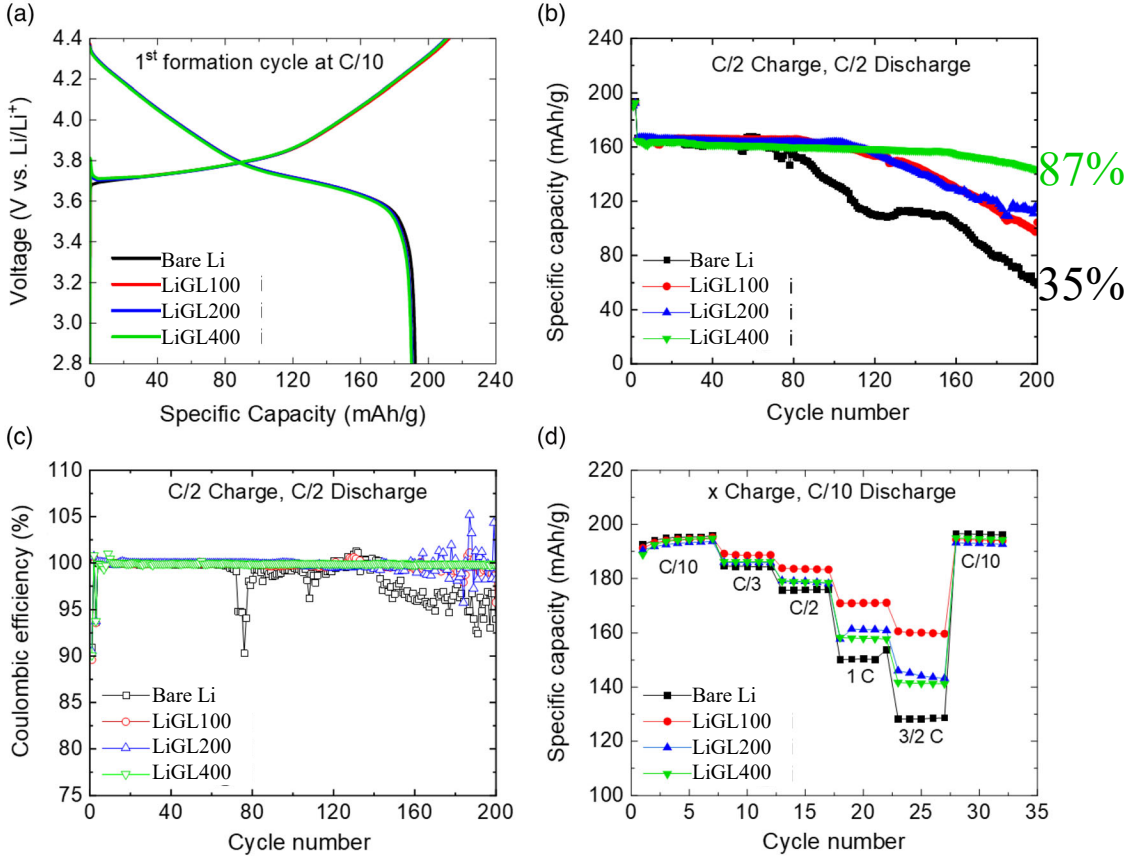


After 500 Li-stripping/plating cycles at 2 mA/cm^2 and 1 mAh/cm^2.

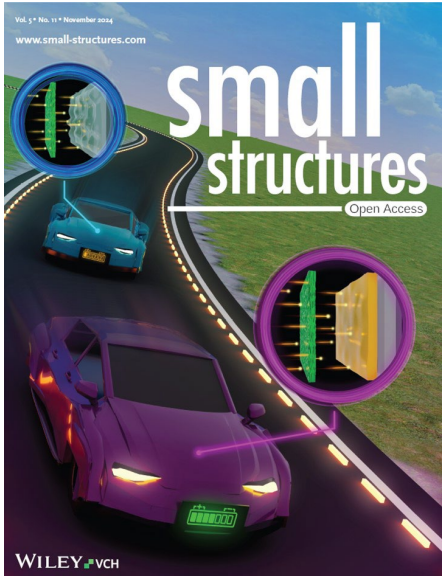
The Promising Resultant Li||NMC LMBs

Li||NMC622

Small Structures 2024, 2400174.

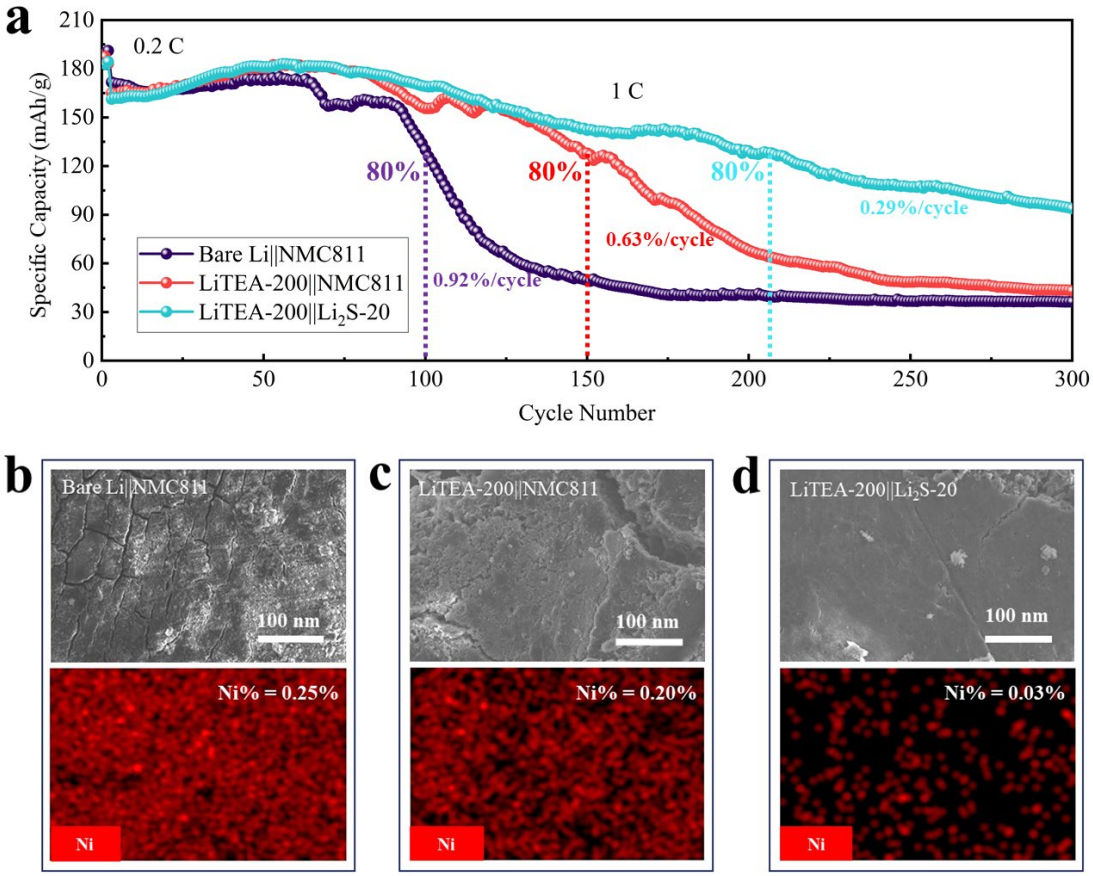


LiGL



Li||NMC811 cells

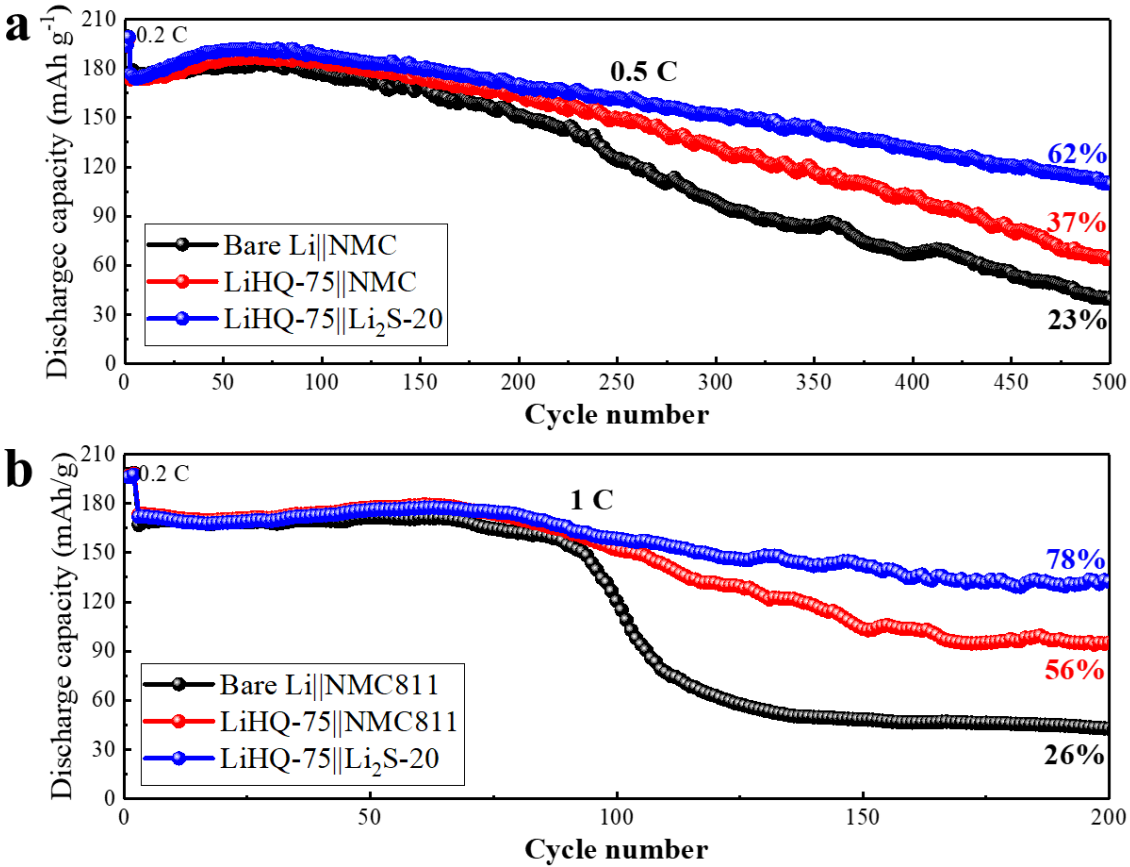
Chemical Engineering Journal 2023, 475, 146156



LiTEA

Li||NMC811 cells

Nano Energy 2024, 128, 109840



LiHQ

Conclusions

- ALD and MLD are two powerful techniques for growing novel coatings in a controllable mode.
- Sulfide coatings via ALD were first reported for tackling issues of NMC cathodes and showed exceptional protection effects.
- Lithicone coatings via MLD were first reported for tackling issues of Li metal anodes and exhibited tremendous potential.
- The resultant modified Li||NMC cells showed very promising performance in long-term cyclability and high energy.

Acknowledgements

UNIVERSITY OF ARKANSAS

Thanks for your attention!

Meng Group